An-Najah National University

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# Chromium Removal and Recovery from Tanneries Effluents

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# COMMITTEE DECISION

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# DEDICATION

To

My Dearest Mother

For Her Kindness and Encouragement

To My Family and To My Friends For Their Encouragement

With My Deep Love And Respect

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# Abstract

Tanning of leather is a traditional industry in Palestine. It is accompanied by the use of tens of chemicals and consequently by the emission of a number of pollutants. Many pollutants need pretreatment before discharging the effluents in order to meet the discharging requirements.

One of the most dangerous tanning pollutants is chromium. The removal and recovery of chromium from the tanning effluents is the main objective of this work. The application of coagulation-precipitation method for the treatment of the chromium in the tanneries effluents was applied in this study. Removal was applied to the effluents of the tanning step in the tanning process (the step to which chromium is added to the hides and skins). Experiments were carried out in Birzeit University/Water Engineering laboratory as well as in one of Hebron Tanneries. Characterization of the tanneries effluents through laboratory analysis were carried out in Birzeit University/Water Engineering Laboratory. Analysis was carried out according to the Standard Methods for the Examination of Water and Wastewater. Recovery was carried out in Hebron tannery. Three coagulants were used to examine the efficiency of removal: MgO, $Na_2CO_3$ and Prestol. MgO showed the best removal efficiency. Experiments showed a 99% removal. The precipitated chromium was then successfully used in the leather tanning and showed a good leather quality as that tanned by fresh chromium.

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# Glossary

- Bating: is the manufacturing step which follows liming and proceed pickling. The purpose of the bating is to delime the hides, reduce swelling, peptize fibers, and remove protein degradation products
- Beamhouse: is that portion of the tannery where the hides are washed, limed, fleshed and unhaired, when necessary, prior to the tanning process
- Biochemical Oxygen Demand (BOD): is a measure of the quantity of oxygen which may be consumed while biologically degrading the organic constituents. The test is carried out over five days and the result expressed as $BOD_5$
- Chemical Oxygen Demand (COD): is a measure of the quantity of oxygen consumed during chemical oxidation of the constituents of an effluent with potassium dichromate
- Deliming: is the process which removes the lime from hides coming from the beamhouse
- Dewatering: is the process of removing a large part of the water content of sludges
- Disposal: is the act of discharging a waste or effluent into the environment
- Eutrophication: is the nutrient enrichment of natural waterbodies leading to excessive growth of algae and weeds so as to ultimately choke the normal aquatic life processes
- Faecal coliforms: are intestinal bacteria. These indicate contamination by manure or sewage
- Finishing: is the final set of processing steps performed on a tanned hide. These operations follow the retan-colour-fatliquor processes, and include the many dry processes involved in converting the hide into the final tannery product
- Full chrome: is used to refer to a tannery process. "Full" is sometimed added to the term "chrome tanned" to emphasize that the leather has not been tanned by the semi-chrome or combination chrome processes
- Grain: can mean: a) the outer, or hair side, of a hide or skin that has been split into layers; or
- b) the pattern visible on the outer surface of a hide or skin after the hair or wool has been removed
- Leather: is a general term for hide or skin which still retains its original fibrous structure more or less intact, and which has been treated so as to be non-putrescible even after treatment with water

- Pickling: is the process that follows bating, whereby the skin or hide is immersed in a brine and acid solution to bring it to an acid condition. It prevents precipitation of chromium salts on the hide

- Pollution; is a state that occurs when assimilative capacity of the environment is exceeded, resulting in illness or death of organisms, and undesirable ecological changes

- Retanning: is the process of subjecting a skin, which has been first more or less completely tanned by one process or one kind or blend of tanning materials, to a second tanning process involving similar or, more usually, different tanning materials

- Total Kjeldahl Nitrogen (TKN): is a measure of the quantity of total nitrogen content, and hence the potential for excessive growth of aquatic plants

- Total solids: refer to both dissolved and suspended solids in the effluent

- Treatment: is the reduction or change in the level of a pollutant

- Turbidity: is a measure of the light-transmitting properties of water. It is a test used to indicate the quality of waste discharges and natural waters with respect to colloidal matter. Colloidal matter will scatter or absorb light and thus prevent its transmission

- Tannage: the application of a tanning agent.

# Chapter One

## Introduction

# 1. INTRODUCTION

Tanning is a chemical process, which converts putrescible hides and skins into a stable material. It is the processing and preservation of animal hides and skins to make leather, it is one of the oldest industries in history. Vegetable, mineral and other tanning agents may be used, either separately or in combination to produce leather with different qualities and properties. In the leather industry, the water demand is very high. The tanning process is accomplished in a different number of steps and phases; each is accompanied by the use of a number of chemicals. About 50% of the chemicals are emitted as strongly polluting wastes that constitute very serious long-term environmental problems.

## 1.1 Problem Definition

Leather tanning industry is recognized as a heavy pollutant process for water, air and soil. The main contaminants include chromium salts, chlorides and sulphur compounds mainly in the form of toxic gas and/or inorganic salts.

Leather tanning is the chemical treatment of raw animal hide or skin to convert it into leather by the use of tanning agents. A tanning agent displaces water from the interstices between the protein fibers and cements these fibers together thus converting raw leather to non-putrefied form. The three most widely used tanning agents are vegetable tannin, mineral salts such as chromium sulfate, and fish or animal oil.

### 1.1.1 Tanning process

Tanning process is the industrial treatment of animal hides comprises the preparation and processing of the raw material by the use of auxiliary chemical products **(Chernicharo and Van Vliet, 1996)**. As a result, the first phases of this process are responsible for the production of large quantities of liquid effluents containing high concentrations of organic matter and also of several chemical products. Among the pollutants present in these effluents are chromium and sulphides, also many other chemicals are of concern such as ammonia, chlorides, detergents, emulsifiers, bactericides, coloring agents etc. Because the uptake of the chemicals used in this industry is never complete in the technological process, so the compounds used in the process form part of the pollution in the effluents.

Different wastewater stream are released, some of them with extreme pH values. In general, the discharged wastewater has a high organic loading (Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)), but additionally contains considerable amounts of chromium salts, sodium sulfides, ammonium sulfide, formic acid etc. Some of these constituents are toxic or carcinogenic. In addition this process creates objectionable odors.

The hides, after the removal of flesh and fat, are treated with chemicals to form a stable, durable material. After tanning, the hides will usually be further processed according to their intended end use.

One of the most important raw materials used in the leather industry is water, which is used, in the entire wet processing units. By the use of classical production techniques and washing processes, large amounts of water are lost and considered as wastewater. There are more than twenty stages in the leather industry start with soaking and end with finishing. Therefore, pollutants at these stages vary quantitatively and qualitatively.

Chromium (III) sulphate has been widely used as a tanning agent in the leather industry **(Panswad et. al, 1995).** Interaction between chromium ($Cr^{3+}$) and collagen leads leather to stabilize and to possess a shrinkage-temperature property of over 100°C. In chrome tanning, only 70-80% of chromium applied is taken up by the leather, and the rest is discharged as waste, inducing an important source of chromium contamination. The biological sludge from the tannery waste treatment has a high content of chromium and can cause accumulation of the metal in the soil. The chromium when accumulated in plants and animals at high levels can generate serious diseases. This is in addition to the large volume of wastewater containing very high chromium concentrations and the difficulties in finding proper disposal a site for the sludge produced. The average concentration of chromium in the tannery-combined effluent is in the range of 70 mg/l **(UNEP IE/PAC, 1991),** with variations between

3000-5000 mg/l in the effluent of the chromium tanning process **(Sengül and Gürel, 1993)**. The maximum allowable limit for discharge effluent containing chromium coming from the tanning leather industry is 2.0 mg/l **(WHO, 1982)**.

## 1.1.2 Tanning in Palestine

In Palestine, there are two kinds of hides and skins that are processed to produce leather. The first type is the cowhide, which are processed to produce leather for shoes industries. The second type is the sheep or goatskins, which are processed to produce leather for clothing and bags. The leather production demand is always increasing to meet the requirements for the market needs.

The tanning industry in the West Bank is located mainly in the district of Hebron in the South, where one can find eleven independent tanneries located next to each other in one neighbourhood in the industrial municipal zone **(Khateeb & Simon, 1998)**. All these tanneries belong to one extended family. Two other tanneries are located in the industrial zone of Nablus district in the north of the West Bank. A new built tannery is located in Salfeet town in the north. Another one is located in Anabta in Tulkarem, but this later tannery has not been studied since the advanced stages in the tanning such as chromium tanning are not reached.

Tanneries in the West Bank are often located in industrial zones near the residential areas and there are a lot of objections against them because of the bad smell released in some process steps. The expansion of the towns in the last few years has reached the industrial areas and some residential houses nowadays are situated very close to tanneries. Therefore, there should be a study and a research about tanning industry for proper management of their sites, reduction of their wastes and a suggestion for a pretreatment and a reuse of the chemicals used in the process if possible.

There are two major negative impacts of the existing tanneries; first is the huge amount of fresh water consumed in the process, second is the generation and release of corresponding amounts of wastewater with significant pollution loads. The tanning process produces wastewater highly loaded with organic, salts and other chemicals used in the process, as well as a high organic loading (BOD and COD). This wastewater has adverse impact on the environment if discharged without proper treatment. Disposal of tanning wastewater to open ditches or valleys can allow its infiltration into the underground down to the ground water aquifers and lead to a pollution of the freshwater resources.

The disposal of wastewater to the sewage system increases the salt concentration of the sewage and makes the treatment and reuse of wastewater effluent in agriculture very difficult. Disposal of the saline wastewater will also affect the biological treatment of the wastewater as it affects the growth of bacteria required in the biological treatment. The inorganic constituents in the effluent will increase the salinity of the soil that then will decrease the yield of the crops and by time will destroy the soil texture. .

### 1.1.3 Hebron's tanneries

The eleven tanneries in Hebron Town are connected to one main manhole from which the wastewater is discharged to the municipal sewerage system. While there are actually no treatment capacities, the effluent of the tanneries, mixed with sewage or wastewater from other industrial effluents, are discharged into wadies, where it runs in open ditches. Farmers frequently use it for irrigation. There are major potential and real health impacts related to this objective **(Khateeb & Simon, 1998)**. All the tanneries suffer from water supply shortages and they have to get their water by tanks at the price of 12 NIS per $m^3$ (around 3 US$).

All of the tanneries in Hebron (except one) process just cowhides. The leather produced from cowhides is mainly used for the shoes industry. The demand on the leather is much higher than the supply and there is a demand for export of leather. But in order to increase their capacities, the tanneries in Hebron would have to expand. This is not possible, due to the fact that actually already almost the whole area is covered with facility-buildings. They also can not step into a new, more qualified market, to tan leather for clothes. This would require more water and more washing and final treatment steps.

In general there is a great objection against the tanneries from the site neighbors in the area where they are located. Despite the fact that these tanneries have been there first, the tanners showed their willing to move to an area which would allow them to extend their capacities and to produce leather with higher quality and higher market value.

## 1.2 An Urgent Study

The tanning industry produces highly loaded organic wastes as it disposes chemicals to the municipal sewerage system. Therefore, it is clear that there is a need for a systematic study to be done to all tanneries in Palestine. This will help in characterizing qualitatively and quantitatively the tanneries effluents and proposing an appropriate method for their disposal. Chrome removal is of a special concern in this study as it can bioaccumulate in residual wastewater treatment plant sludges and make sludge disposal difficult. This study is urgent for the following reasons:

i. Leather tanning is considered as one of the industries that impart environmental problems due to the qualities and quantities of chemicals used and consequently emitted in this process.

ii. Leather tanning is considered as one of the industries that helps in developing the country's economy. Since the tanneries produce leather either for clothes industry or for shoes industry, and since the tanneries are supposed to provide leather for 554 shoes factories as well as 3 clothing and bag factories in Palestine **(ABC, 1997)**. The demand for leather is expanding and there is a need to produce more high quality leather.

iii. There is no previous systematic study done before in Palestine about this industry concerning the nature and characteristics of the tanneries effluents and concerning determining an appropriate method for the disposal of such effluents.

iv. The absence of any treatment method or treatment plants for the effluents of the existing leather tanneries.

v. The importance of this study will be much higher in the district of Hebron, since there are eleven tanneries located in the same industrial zone, and the large amounts of effluents that are discharged into the sewage system. Hence the existence of a treatment method is very important; also the application of any treatment method will be much useful and easier because of the closeness of the tanneries to each other.

vi. As an application to the clean technology concept. This concept states that reduction of a pollutant at the source is much more efficient than treatment of the combined effluent.

vii. The need for the existence of safety measures and awareness in the tanneries as well as proper handling of equipment and chemicals used in the tanning process.

## 1.3 Goal of the Study

The main goal of this research is to define the most appropriate method for chromium removal and recovery from the tanning process effluents of the existing tanneries in Palestine.

## 1.4 Objectives of the Study

The main objectives of this study are to:

1. Build a database of tanneries effluent characteristics (quantitatively and qualitatively).
2. Select on the basis of literature data, the most suitable process by which chromium is removed and recycled from the effluents of the tanneries.
3. Introduce the clean technology concept and to apply it on the tanning industry.
4. Determine the feasibility and efficiency of removing and recycling the chromium.

## 1.5 Layout of the Study

This study will be divided into five chapters:

- Chapter one (this chapter) is a general introduction and the urgent study needed
- Chapter two focuses on the literature survey about tanning process industry. This chapter includes the description of the tanning process, step by step description. the chemicals and pollutants accompanied by this industry. It also includes the environmental impacts of the tanning process in general and the

impacts of chromium in particular. It includes the methods used to remove the pollution caused by chromium compounds.

- Chapter three is the methodology followed in this study, this includes distribution of a questionnaire, sampling and lab analysis, laboratory experiments for the removal of chromium and scaling up the results obtained in the lab for the removal and recycling of chromium in an existing tannery in Hebron. The selection of the method for the chromium removal is chosen to satisfy the clean technology concept.
- Chapter four lists all the results obtained from chapter three as well as the discussion of these results.
- Chapter five summarizes the conclusions resulted from this study and put forward recommendations for further work needed to be done for the continuation in this field. It also includes the general safety measures in tanneries such as using equipment and machinery, handling of chemicals used in the tanneries and the awareness of the chemicals generated in tanning processes.

# Chapter Two

# Literature Survey

# 2.1 Description of the Tanning Process

## 2.1.1 Introduction

Tanning is the process by which animal hides and skins are converted into leather. In an age of metals and synthetics, leather has somehow kept its place as a product of superior quality, feel and value. Leather leaves the original hide fibrous structure more or less intact and is imputrescible even after exposure to water. The hair or wool may or may not have been removed. Certain skins without the hair removed are termed "fur". Outer covering of large animals, *e.g.* mature cattle is described as hides and those from small animals, *e.g.* sheep, as skins **(Korsak, 1998)**.

Leather is one of the oldest commodities known. The first leather was made when hides were treated with vegetable extracts to make them weather resistant. The art of leather manufacturing antedates by centuries any scientific knowledge of the chemistry involved. Probably the greatest single advance in the leather industry was the practical application of the chrome process of tanning introduced in 1893. More than 90 percent of the world's output of leather is chrome tanned **(Austin, 1985)**.

Leather is not one product, but a great number of products ranging from very utilitarian heavy-duty boot leather to specialty fish and reptile skins for the fashion trade. There is a steady supply of raw materials and a ready market for finished products.

## 2.1.2 Tanning processes

Hides and skins comprise three distinct layers. These are the outer thin layer of epithelial cells called the epidermis, the thick middle layer called the corium or dermis and a subcutaneous adipose or flesh layer. The epidermis and flesh layers are removed before tanning and the corium is tanned into the leather **(UNEP IE/PAC, 1991)**.

Raw hides and skins are generally obtained in fresh, dry-salted or wet-salted conditions. Then leather is produced from hides and skins in three stages as shown figure 2.1

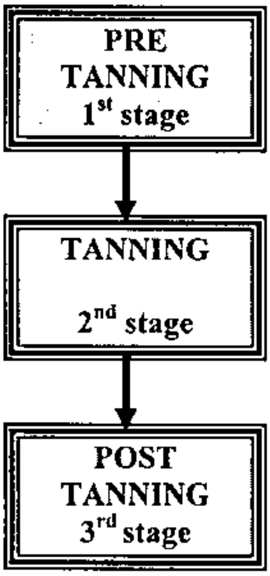

Fig.2.1 Leather production stages **(UNEP IE/PAC, 1991)**

The following part is a detailed description of the leather production stages described in figure 2.1 as well as the chemicals used and wastes produced.

***1) Pretanning***

This stage is sometimes called Beamhouse **(UNEP IE/PAC, 1991)**.

At this stage the hide is prepared for tanning by cleaning and conditioning, and by ensuring the correct moisture content.

At this stage some constituents such as hair, flesh, fat and some interfibrillary material are removed, leaving a concentrated network of high-protein collagen fibers. This stage is carried out in five different steps, these are:

Soaking

Soaking may be carried out in a pit, paddle or drum (or a combination of these) to rehydrate the skin and reverse the cure process which consists of drying or salting of the skin in order to protect temporarily the natural material from putrefaction. As a result of curing process the skin loses moisture. Dirt, blood and dung are also removed in this step.

The chemicals used in this step are sodium hydroxide, sodium sulphide, sodium hypochlorite and/or wetting agents, emulsifiers, surfactants and enzyme preparations.

The main wastes produced in this step are BOD, COD, SS, salts and organic N **(UNEP IE/PAC, 1991)**.

Liming and Unhairing

The most effective way to remove the hair is based on a very selective breakdown of the disulphide bonds in keratin by sulphide ions in basic medium. Lime blended with sodium sulphide is traditionally used to loosen wool or hair, or to dissolve these into a pulp. Additionally, the process opens the fiber structure and "plumps" the hide. The duration of the process may vary from 18 hours to 7 day. This process is responsible for the major part of the COD load from the tannery.

The chemicals used in this step are calcium hydroxide (lime) or some caustic soda, sodium sulphide, sodium sulphydrate, enzymatic preparations (increasingly used). The major wastes produced are BOD, COD, SS, DS, alkalinity, sulphides, organic N and ammonia N **(UNEP IE/PAC, 1991)**.

Fleshing

Limed hides are fleshed manually or mechanically to remove the adipose tissue from the flesh side of the hide. In some cases fleshing is carried out immediately after soaking (green fleshing) **(UNEP IE/PAC, 1991)**.

There are no chemicals used in this operation. And the wastes produced are limed fleshings (fat containing limed organic matter).

Deliming and bating

The removal of lime from the pelt is necessary to avoid interference with the subsequent tanning stage. Thorough washing is followed by the application of neutralizing chemicals. Washing traditionally requires copious quantities of water, often from a water valve left open for a period. Water discharge in such case is not constant or measured.

Bating is an enzymatic process, which has a pronounced effect on the grain of the pelt, and on the general run and stretch of subsequent leathers.

The chemicals used in this step are acids (sulphuric, hydrochloric, lactic, formic, boric and mixture), acidic salts, ammonium chloride or sulfate. The wastes produced are characterized by high concentrations of $NH_3$, BOD, COD, DS and ammonia N **(UNEP IE/PAC, 1991)**.

Pickling

The final pretanning operation is the adjustment of the pH of the pelts, thereby sterilizing the skin, ending the bating action, and improving penetration of the subsequent tanning material.

Common salt (sodium chloride) or sodium sulphate; acid (sulphuric, hydrochloric, acetic or formic, or mixtures) are the main chemicals used in this step **(UNEP IE/PAC, 1991)**.

### *2) Tanning*

Tanning is the chemical stabilization of the collagen network.

Using natural or synthetic chemicals stabilizes collagen structure of the hide. An agent displaces the water and combines with the collagen fibers, greatly increasing resistance to heat, hydrolysis and microbial degradation. In addition, tanning imparts a particular "feel" to the resulting leather. A variety of chemical agents are available, with chrome being the most commonly used.

The majority of leathers today are chrome tanned in drums from 4 to 24 hours. While vegetable tannage has been eclipsed by chromium as the major tanning process, it is still employed for sole and saddlery and some specialty leathers. It may also be used as part of a combination process. Duration of the process is from 1 day to 6 weeks **(UNEP IE/PAC, 1991)**.

Tanning step can be accomplished by the use of chromium as a tanning agent separately or by the use of vegetable tannins as a tanning agent separately or by using the combination of both tanning agents. The following part describes the combination tanning process:

Combination tanning: chrome-vegetable tanning

Leather is a material of infinite variety of form, texture, appearance and use. Diversity of use and property of leather needs a skilful and scientific technique to make it. A proper understanding and adjustment of a series of coordinated reactions obtain the desired properties of leather. Each type of tanning, chrome or pure vegetable tanning results in leather with certain characteristic properties. Vegetable tanned leather is soft and full with a good feel and strength. The full chrome leather is tough, durable and stable to heat. It is possible to impart the good qualities of different kinds of tanning to the same leather by pre-tanning the pelt with one kind of tanning material and retanning the same with a different tanning material, i.e., by combination tannage. Combination tannage not only influences the properties of the end product but it sometimes reduces the time of tanning, thus lowering operation costs. Thus, combination tannages are very valuable. Numerous combination tannages of chrome, iron, aluminum, sulphur, vegetable, syntan, sulphite cellulose, formaldehyde and oil have been practically tested and used **(Nayudamma, 1991)**.

Chrome-vegetable combination tannage may be carried out in three ways **(Nayudamma and Ranganathan, 1991)**:

(a) Chrome pre-tannage and vegetable tannage
(b) Vegetable pre-tannage and chrome tannage
(c) Simultaneous chrome-vegetable tannage

The sequence and intensity of tanning agents have an influence on the quality and properties of leathers **(Nayudamma, 1991)**.

The main chemicals used in this process are chrome tanning salts, vegetable tans, syntans, sodium bicarbonate and masking agent. The main wastes produced are BOD, COD, SS, DS, acidity, salts, chrome, vegetable tans, syntants and other salts **(UNEP IE/PAC, 1991)**.

### *3) Post - Tanning*

#### *3.1) Mechanical operations*

After tannage, certain mechanical operations may occur in order to level surface of the irregular natural material, these operations are:

Sammying by machine (pressurized rollers) to remove excess moisture;

Splitting by machine, if not carried out in the lime condition;

Shaving whereby the substances are leveled, the surplus material yielding a waste of small fragments

Trimming

These operations yield a combination of solids, squeezed-out water, and unfixed tanning chemicals.

### *3.2) Post tanning Wet- work*

This involves further processing of the stabilized collagen network and may comprise a further tannage (*e.g.* with combinations of chrome, vegetable, and glutaraldehyde or syntan agent) when special characteristics such as perspiration resistance are required. Conditioning, softening, dyeing or bleaching may also be carried out.

### *3.3) Drying and Finishing*

The leathers are sammied to remove moisture then dried. The final finishing processes include mechanical treatment of grain and flesh, followed by application of surface finish.

Different chemicals are used depending on the final special leather characteristics required. The wastes produced are chrome split, shavings, chrome trimmings, solvents, remainder of finishing agents **(UNEP IE/PAC, 1991)**.

Figure 2.2 is a schematic of the tanning process, indicating waste streams in both air and water environment.

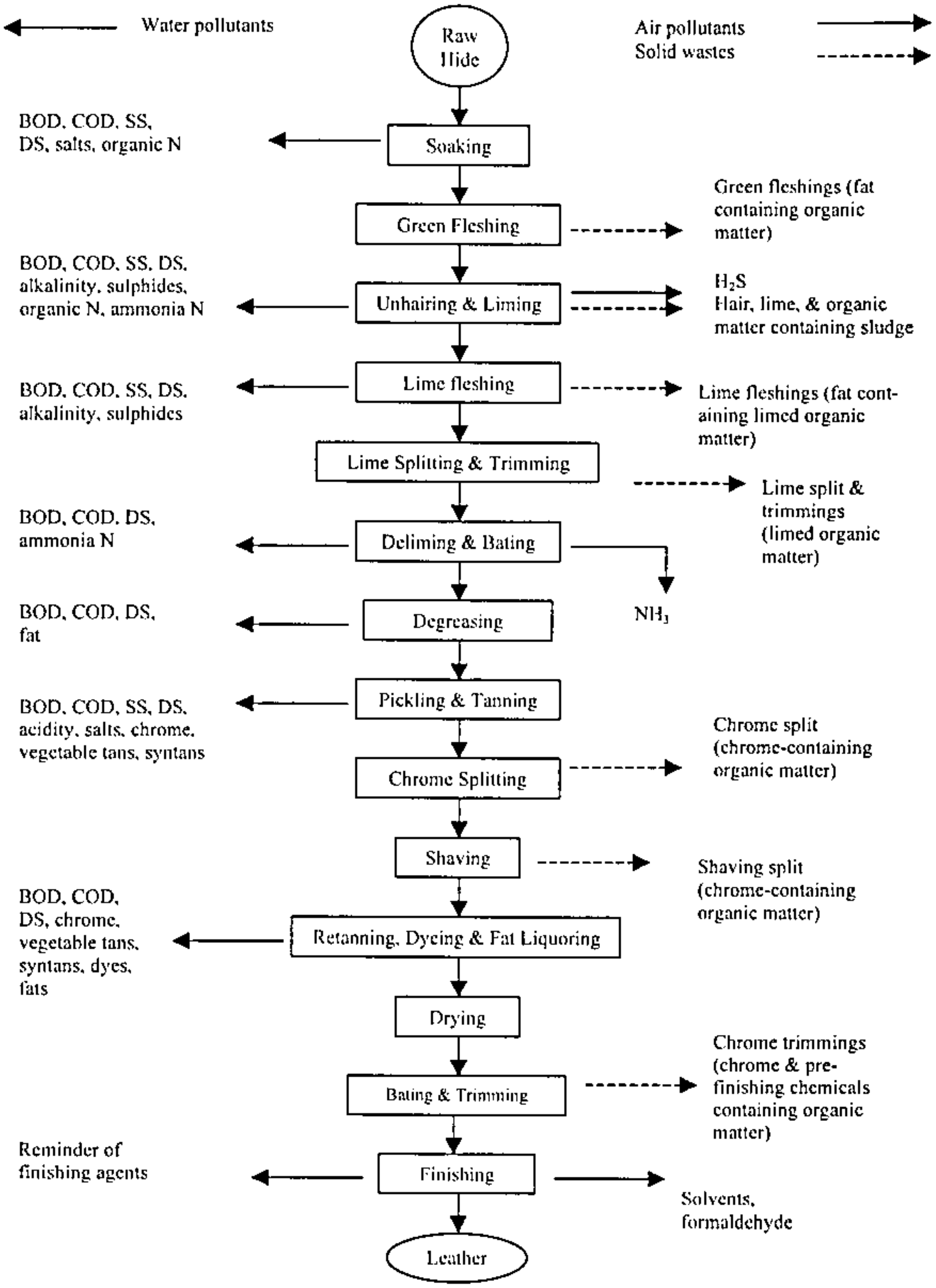

Fig.2.2. A Schematic diagram of the tanning process **(UNEP IE/PAC, 1991)**

# 2.2 Tannery Waste: Composition and Characteristics

## 2.2.1 Chemicals used in the tanning process

The tanning process uses a significant amount of chemicals. According to the purpose of use, the chemicals comprise three groups of materials: general purpose, basic tanning and performance. Also the major chemicals can be divided according to their chemical functional properties such as sulfur compounds, chlorides, chrome salts and others. A list of all chemicals used is shown in table 2.1

| **Chemicals/Material** | **Formula of chemicals** | **Amount used in (kg) per 100 kg of raw hides** |
|---|---|---|
| ***1. General purpose chemicals*** | | |
| Sodium sulfide | $Na_2S$ | 3.0 |
| Calcium hydroxide | $Ca(OH)_2$ | 4.5 |
| Hydrochloric acid (conc.) | $HCl$ | 0.3 |
| Ammonium sulfate | $(NH_4)_2SO_4$ | 2.0 |
| Sodium bisulfate | $NaHSO_4$ | 1.5 |
| Sodium chloride | $NaCl$ | 10.0 |
| Calcium formate | $Ca(COOH)_2$ | 2.0 |
| Sulfuric acid (conc.) 96% | $H_2SO_4$ | 4.0 |
| Sodium carbonate | $Na_2CO_3$ | 2.0 |
| Sodium sulfite | $Na_2SO_3$ | 2.0 |
| ***2. Basic Tanning Materials*** | | |
| Chrome salts | $Cr_2(SO_4)_3$ | 10.0 |
| Vegetable tanning materials | | 3.0 |
| ***3. Performance Chemicals*** | | |
| Bates | | 0.8 |
| Bactericides | | 0.3 |
| Syntans | | 3.0 |
| Fat liquors | | 4.0 |

Table 2.1 Chemicals used in the tanning process **(UNEP IE/PAC, 1991)**

## 2.2.2 Wastes generation

### A. Liquid waste generation

Due to the different chemicals used in the leather manufacturing process, the composition of tannery effluent is very complex. The amount of chemicals and tanning materials per unit of hide vary within a wide range due to the variety of recipes and changes in fashions, colours required, etc. **(UNEP IE/PAC, 1991)**.

During the conventional way of chrome leather production, about 50% of the chemicals are emitted as strongly polluting wastes which with chrome, chlorides, sulfates and sulfides constitute a very serious long term environmental problem

In the leather industry, the specific water demands per unit finished product is very high, tanneries are among the most intensive plants. The quantity of water depends, to a slight degree, on the type of hides and the mechanical and chemical methods used in tanning. **GTZ (1989)** reported that, the required amount of water per ton of rawhide is 100 $m^3$. The actual water demand in the factories is usually higher than this as it includes the water used to clean the machines and workshops, as well as in the staff welfare rooms.

Table 2.2 shows the composition of a typical combined tannery effluent that is not treated. It is characterized by high oxygen demand, high sulfide (nuisance odor), sulfate concentration, high salt content, and strong alkalinity. It also contains a high level of suspended solids, and a high load of chrome **(UNEP IE/PAC, 1991)**.

Levels of contaminants concentration experienced in an actual tannery will vary to some extent from these values depending on water use. The generally accepted range of water use is 25 - 80 $m^3$/ton of hide processed **(UNEP IE/PAC, 1991)**.

| Parameter<br>( Chrome Tannage ) | Value<br>(mg/l) |
|---|---|
| pH | 9 |
| Total solids | 10 000 |
| Total ash | 6 000 |
| Suspended solids | 2 500 |
| Settled solids (2 h) | 100 |
| $BOD_5$ | 900 |
| COD ($K_2Cr_2O_7$) | 2 500 |
| Sulphide | 160 |
| Total nitrogen | 120 |
| Ammonia nitrogen | 70 |
| Total Chrome (Cr) | 70 |
| Chloride ($Cl^-$) | 2 500 |
| Sulphate ($SO_4^{-2}$) | 2 000 |
| Ether extractable | 200 |

Table 2.2 Composition of a typical untreated combined tannery effluent **(UNEP IE/PAC, 1991)**.

While such a table is a useful indication of the orders of magnitude involved, it can not be used for the design of a treatment plant. The composition of tannery effluent depends in each case on the types of processes in use at the time, and on the level of water consumption. In many situations it is better to treat the individual process effluents separately.

## B. Solid wastes generation

Tanning process is not only accompanied by the discharge of wastewater characterized by high levels of contaminants, but also a generation of considerable quantities of solid wastes is involved. Based on dry basis, Table 2.3 presents the solid wastes generated in complete chrome/finish tanneries:

| Type of Waste | Amount (kg/t of processed hides) |
|---|---|
| Scrap products | 18 |
| Waste with heavy metals | 38 |
| Wastewater screenings with heavy metals | 4 |
| Sludges with phenol and heavy metals | 12 |

Table 2.3 quantities of solid wastes (on dry basis) generated in complete chrome/finish tanneries **(El-Hinnawi, 1995)**

## 2.3 Discharge Conditions

The international limits of tanning industry effluents that can be discharged directly or indirectly to the municipal sewage should satisfy the values shown in table 2.4 **(UNEP IE/PAC, 1991)**

| **Parameters** (mg/L unless other) | **Brazil** | **India** | **Italy** | **Nether lands** | **USA** | **(Korsak, 1998)** |
|---|---|---|---|---|---|---|
| pH units | 5.0-9.0 | 5.5-9.0 | 5.5-9.5 | 6.5-8.5 | 6.0-9.0 | 6.0-9.0 |
| $BOD_5$ | 60 | 30 | 250 | 5 | 40 | 120 |
| COD | - | 250 | 500 | - | - | 250 |
| Suspended Solids | - | 100 | 40 | 80 | 60 | 150 |
| Sulphides | 1.0 | 2.0 | 2.0 | - | - | 0.1 |
| Chrome (III) | - | 2.0 | 4.0 | - | - | - |
| Chrome (VI) | - | - | 0.2 | - | - | 0.1 |
| Total Chrome | - | - | - | 0.05 | 1.0 | 1.0 |
| TKN | - | - | - | 3.0 | - | - |
| Oil/Grease | 20 | - | 30 | - | - | 30 |

Table 2.4 Comparison of discharge standards for tannery wastewaters for several countries **(UNEP IE/PAC, 1991& Korsak, 1998)**
Note: (-) not reported

## 2.4 Environmental Considerations

### 2.4.1 Overview

The major public concern over untreated tanneries discharges has traditionally been about odours and water pollution **(UNEP IE/PAC, 1991)**. Recently, pollution issues, and particularly health and safety issues are the main concern to the public. These issues arise from the increasing use of synthetic chemicals such as pesticides, solvents, dyes and finishing agents, as well as from the use of newer processing chemicals. These substances are frequently toxic and persistent, and affect both human health and the environment.

### 2.4.2 Consideration of Some Specific Impacts

#### a. Effect on surface waters

Untreated tannery wastes in surface waters can bring a rapid deterioration of their physical, chemical and biological qualities. Wastes may give rise to noxious odours from the decomposition of organic matter. Their decomposition may deplete the dissolved oxygen in the water that is vital for aquatic life. The water may also become saline and hard due to the presence of inorganic salts, and acquire some toxicity from the chromium. sulfides and ammonia in the waters. Release of nitrogenous compounds will stimulate aquatic plant growth, contributing to eutrophication of water bodies. Pathogenic microorganisms may also occur in watercourses that receive tannery waste discharges. Furthermore, due to turbidity, photosynthesis may be restricted, affecting the primary link in the food chain **(UNEP IE/PAC, 1991)**.

The biochemical Oxygen Demand (BOD), chemical Oxygen Demand (COD), pH, sulfide, ammonia, nitrate, total kjeldahl nitrogen, phosphate, faecal coliforms, chromium, aluminum, colour, sulfate, chloride, pesticides and suspended solids are common waste water characteristics **(UNEP IE/PAC, 1991)**.

#### b. Effect on land

Soil has certain capacity to neutralize pollutants. Treated effluent can accordingly be used to irrigate crops. However pollutant levels need to be carefully controlled. Damaged soil structure leads to loss of agricultural production capacity, and to accelerated erosion. Deteriorated land takes a long time to recover **(UNEP IE/PAC, 1991)**.

Disposal of municipal and industrial wastewater on land is an old practice. However some wastes may affect soil fertility, or they may contaminate sub-surface water due to the high salt content and toxic components. Stagnation of wastes on land may create an odour nuisance.

### c. Effect on groundwater

Groundwater contamination occurs when wastewater and chemicals seep through the soil from unlined ponds, pipes and drains, or from dumps and spills. Groundwater may take a long time to clean itself, as it moves slowly and is out of contact with the air. For many users, groundwater may be the only reliable source of water supply **(UNEP IE/PAC, 1991)**.

### d. Effect on waste dumps

Industrial waste dumps may contain hazardous chemicals. They are frequently highly noxious owing to odorous wastes. The presence in dumps of unwashed containers from industry may result in the poisoning of people who try to re-use such containers without realizing the danger of residual chemicals **(UNEP IE/PAC, 1991)**.

### e. Effect on sewers and sewage treatment works

In addition to the deposition of solids, raw unsettled tannery wastewaters can cause encrustation of calcium carbonate in sewers. Excessive sulfide content may accelerate corrosion and deterioration of concrete or cement. High sulfate levels are also deleterious to concrete.

Very high pollution loads, particularly in conjunction with toxic substances such as chrome, can interfere with the biological processes of sewage treatment plant. Where no treatment occurs, these pollutants may damage the ecology of the receiving waters near the sewer outfalls **(UNEP IE/PAC, 1991)**.

### f. Effect on air quality

Biological decomposition of organic materials, as well as sulphide emissions from wastewaters, are responsible for the characteristic objectionable odours from tanneries **(UNEP IE/PAC, 1991)**.

The following are important potential sources of odour

- sulphide emissions from de-hair and waste treatment;
- ammonia emissions from unhairing and delime liquors;
- fleshings.

### g. Effect on human health

Direct contact with some industrial chemicals can cause disability, illness and death. Even relatively minor exposures, if they occur frequently, can eventually build up the toxic levels **(UNEP IE/PAC, 1991).**

Vapors from degreasing and finishing solvents are obvious sources of exposure. Some solvents have relatively high toxicity and should be carefully controlled. The European Commission (EC) has listed leather dust as a potential carcinogen. The unskilled handling of pesticides within the plant, as well as the handling of treated hides, can expose workers to toxic hazards.

Chemical accidents and spills can also be sources of harmful human and environmental exposure. Such events usually occur when insufficient care has been taken in packaging, transport, storage and handling.

While the hazards of traditional tanning agents are understood by the industry, there is less experience with alternatives. These are designed to have lower environmental impact, but no chemical is totally safe. For example evidence is emerging that high levels of aluminum in drinking water may contribute to human illness. Also Titanium is listed by the EC as a toxic substance.

### h. Other effects

A variety of other minor effects such as excessive noise, air emissions from open burning or other operations, and unsightly visual impacts may unnecessarily address the tanning industry as a bad neighbor.

## 2.4.3 Elaboration of Some Particular Environmental Issues

Due to the potential toxicity of some of the chromium chemical compounds, **chromium** is controversial chemical. Depending on its chemical state it has various levels of impact on humans, aquatic life and terrestrial plants, with some ability to move between media.

**Sulfide/sulfate** combinations have a variety of potential health and environmental impacts and cause damage to structures. Their discharge should be limited where possible.

Excessive **nitrogen** is known to cause eutrophication of surface waters and nitrate contamination of groundwater. Some forms of nitrogen, such as ammonia, are toxic to fish. There are several different sources of added nitrogen in a tannery, the major one being the use of ammonium sulfate in delime **(UNEP IE/PAC, 1991)**.

**Sludge disposal** is probably an important factor to reduce the undesirable effects that follow improper dumping practices. Groundwater contamination from unsealed dumpsites is the major concern, but surface runoff may also be a serious problem. The agricultural re-use of sludge is not recommended as it contains different levels of chromium.

The increasing use of insecticides and biocides for hide preservation presents serious problems for the subsequent tannery operations. Manual handling of preserved hides can poison workers.

The washout of pesticides from the hides during tannage can cause wastewater to exceed permitted levels of these chemicals.

## 2.5 Environmental Impacts Considerations by Chromium Compounds

### 2.5.1 Overview

As mentioned before. The major concern of this study is chromium. Its occurrence, availability, fate, environmental impacts as well as its removal methods is to be covered in the following part

### 2.5.2 Occurrence, availability and Fate of Chromium in the Environment/Transport and Distribution

Chromium is obtained from the ore chromite ($FeCr_2O_4$). Chromium ion exists in different oxidation states, these include (0), (III) and (VI) states.

Chromium is present in nature in low concentrations. It is introduced from point sources as mining area and industries in aqueous forms. It can also be airborne transported as chromium oxides which penetrate deeply into the respiratory tract **(Sultan, 1999)**.

Under low oxygen concentrations and general reduction conditions, hexavalent chromium is converted to trivalent chromium, which is ready to be adsorbed to organic and inorganic surfaces. For this reason, trivalent is more commonly found in nature. Total chromium concentration in solution is equal to the sum of Cr (III) and all Cr hydroxides **(Sultan, 1999)**.

Industrial effluents containing chromium are emitted into streams and the air, if it is present in large quantities, the hexavalent chromium may be reduced by, and the trivalent chromium adsorbed on, the particulate matter. If it is not adsorbed, the trivalent chromium will form large, polynucleate complexes that are no longer soluble **(UNEP/ILO/WHO, 1988)**. The transport of chromium in the environment is summarized in figure 2.3

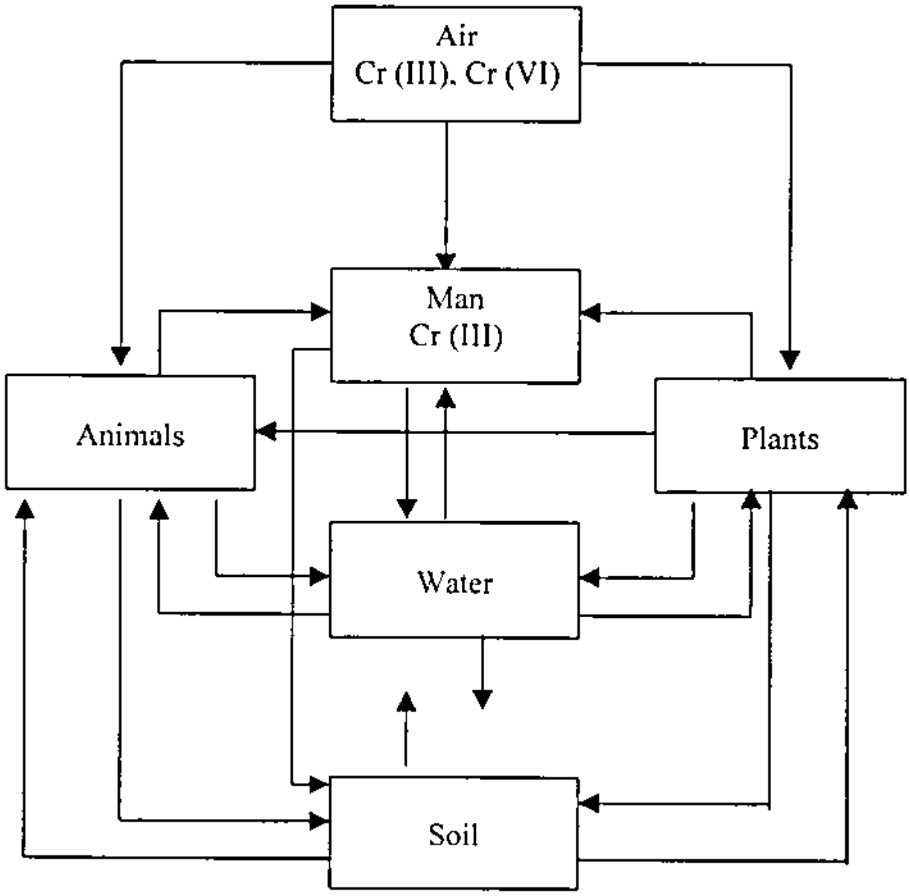

Fig.2.3 Environmental Cycling of Chromium **(UNEP/ILO/WHO, 1988)**

### 2.5.3 Health effects on human and animals

Chromium is an essential metal for human and most mammalian species **(Sultan, 1999)**. Its absence may affect lipid and carbohydrates metabolism. Biologically active chromium is found in the form of dinicotinic acid glutathione complex and is called Glucose Tolerance Factor (GTF). GTF is very essential in maintaining the glucose homeostasis and for production of the hormone insulin. But higher amounts of chromium are considered toxic and have carcinogenic effects on lever and kidney

### 2.5.4 Chromium effects

A- Acute toxic effects

In adults, the lethal oral dose of soluble chromate is considered to be 50-70mg/kg of body weight. The clinical features of toxicity are vomiting, diarrhea, haemorrhagic diathesis, and blood loss into the gastrointestinal tract causing cardiovascular shock. If the patient survives about 8 days, the outstanding effects are liver necrosis, tubular necrosis of kidneys, and poisoning of blood-forming organs **(UNEP/ILO/WHO, 1988)**.

B- Chronic toxic effects

The important features of the chronic effects of trivalent and hexavalent chromium are changes in the skin and mucous membranes, and allergic dermal and broncho-pulmonary effects. Important systemic effects occur in the kidneys, liver, gastrointestinal tract, and circulatory system **(UNEP/ILO/WHO, 1988)**.

## 2.6 Chromium Removing Processes

### 2.6.1 Overview

Most chromium tanning technologies are inefficient due to the low levels of chromium fixed in the tanning bath, coupled with the bleeding out of the chrome in subsequent processes **(UNEP IE/PAC, 1991)**. Developments to reduce chromium discharge are focused on:

### *i. High chrome exhaustion techniques*

Chrome fixation is favored during tannage by short float, increased temperature, increased time of tanning, increased basification, and decrease in neutral salts **(UNEP IE/PAC, 1991)**. This idea is explained in details in the clean technology part of this study.

### *ii. Chrome tannage recycle*

In addition to a saving in chemicals (up to 20% of chrome used), recycling achieves a reduction in salinity of the waste effluents **(UNEP IE/PAC, 1991).** This point is discussed in details in the clean technology part.

### *iii. Chrome precipitation and recovery*

The chrome bearing liquors is treated with alkali to precipitate the chromium as hydroxide that is the redissolved in situ and reused **(UNEP IE/PAC, 1991).** Due to the advantages of this method (to be shown later), it will be the treatment method used in this study.

## 2.6.2 Methods

The following section will discuss the methods used either to remove the chromium from the tanneries effluents or to reuse the chromium after its removal (to recover chromium).

### 1. **Chromium recovery and recycling by coagulation / precipitation**

**(Panswad et. al, 1995)** defined Chromium recovery to be the separation of chromium from the spent liquor by precipitation, then redissolving the chromium sludge for reuse.

This method involves the recovery of Cr (III) from tannery liquors and its reuse, the recovery is applied to the chromium liquor (chromium producing step).

In conventional chrome tanning processes 20-40% of the chrome used is discharged into wastewaters. In this method 95-98% of the waste $Cr^{+3}$ can be recycled.

Tanning of hides is carried out with chromium sulphate ($Cr_2(SO_4)_3$) at a pH of 3.5-4.0. According to **Panswad et.al (1995)** study, the solution was collected after tanning and screened to remove particles and fibers that have come from the hides. Chromium present in the tanning solution is precipitated as chromium hydroxide precipitation ($Cr\ (OH)\ _3$) by the use of two alkalis, i.e., magnesium oxide (MgO) and sodium carbonate ($Na_2CO_3$). Precalculated quantities of both precipitation reagents were then added with stirring for two hours, after which sedimentation study was taken. After the settling process, the supernatant was decanted and the sludge was dissolved in a calculated quantity concentrated sulfuric acid ($H_2SO_4$) until a certain pH is reached. The produced liquor then contains ($Cr_2(SO_4)_3$) and ready for reuse.

The following chemical reactions are involved in this treatment:

$Cr_2(SO_4)_3 + 3\underline{MgO} + 3H_2O \quad 2Cr(OH)_3(\text{ ppt}) + 3MgSO_4$

$Cr_2(SO_4)_3 + 3\underline{Na_2CO_3} + 3H_2O \quad 2Cr(OH)_3\ (\text{ ppt}) + 3Na_2SO_4 + 3CO_2$

$2Cr(OH)_3(\text{ ppt}) + 3H_2SO_4 \quad {}_2(SO_4)_3 + 6H_2O$

**Optimum conditions for precipitation of chromium**

According to **(Panswad et. al, 1995)** study it was found that precipitation using MgO resulted in a removal efficiency exceeding 98% with a sludge volume of 220ml/L and one hour settling time. In the same study, it was found that precipitation by using $Na_2CO_3$ resulted in removal efficiency of 98% but with sludge volume of 540ml/L and 19 hours settling time. As a result the later treating regent was less attractive due to the further necessity of a dewatering unit. Besides, the settling process is too long, that the precipitate then became aged, resulting in a growing insolubility of the substance due to the transformation of hydroxide to mixed-oxides complexes.

The precipitation of chromium is relatively simple. The success of the total operation depends more on the ability to collect the chrome liquors for further treatment **(UNEP IE/PAC, 1991)**

Further researchers, **Sengül and Gürel, (1993)**, worked on the same topic. The main purpose of their study was to remove sulfur and to pretreat organic materials exist in tanneries effluents. During chemical precipitation applied after sulfur treatment, chrome removal was also obtained. The removal of chromium was carried out by the addition of a number of coagulants such as $MnSO_4$, $FeSO_4$, $FeCl_3$ and alum.

According to **(UNEP IE/PAC, 1991 and UNEP, 1994)** there are several techniques for chromium recycling, these are:

1. Direct Recycling of Chrome Tanning Float
2. Recycling After Precipitation
3. Tanning Products that Improve the Exhaustion Rate

These techniques are explained in more details in **Appendix one.**

Recovery of chromium used in the tanning process is feasible. The economy of the process is affected by the value of chromium chemical itself and also the possibility of its reuse within the plant and its concentration

## Other methods:

### 2. Ion exchange process

This method is an ion exchange physiochemical process for selective removal, recovery, and reuse of chromium. The process deals with the "segregated" streams of spent tannery baths and related leather-washing waters **(Petruzelli et. al, 1995).**

The process namely, IERECHROM (Ion Exchange REcovery of CHROMium) is based on the use of a macroporous carboxylic resin, allowing for removal and separation of almost pure (>99%) chromium from other interfering metals (i.e., Fe(III), Al(III)) and organic compounds for reuse.

During regeneration steps, chromium and aluminum are separated and the latter can be reused as coagulant in the general wastewater treatment plant. Chromium is recovered as chromate at an average concentration of about 1700 mg/L, and it could be reused (after makeup) in the plating industry or in the same tanneries after reduction to Cr(III). A final polishing step of the resin allows for ferric sulphate recovery and reuse as flocculating agent.

On the basis of the adoption of this process, the centralized tannery wastewater treatment stations would generate residual sludges with minimized chromium content thus reducing its environmental impact. Detoxified sludges could then be used as soil amendments, used in compost formulation, or directly applied to agricultural land.

Assuming the landfilling costs of toxic sludge disposal as a reference, the economic evaluation of the reference process indicated the overall costs of the proposed ion exchange based technology is about 3 times lower **(Petruzelli et. al, 1995)**.

### 3. Bipolar electro-chemical precipitation process

This process is a method for chromium removal using the electro-chemical precipitation (ECP) process **(Kongsricharoern and Polprasert, 1995)**. This process was found to be feasible in treating high strength chromium wastewater. The electro-chemical precipitation unit, operated in the bipolar mode, had six steel plates including the anode and cathode and was supplied with DC power. The chromium removal efficiencies in the bipolar ECP units are higher than 99%

The mechanisms of chromium removal in the ECP unit were found to be reduction of Cr (VI) to Cr (III) ions, incorporation of the Cr (III) ions into the complex Fe compounds and precipitation. The main compounds of the precipitated sludge were identified as maghemite ($Fe_2O_3$) and chromite ($FeCr_2O_4$) whose percent contents in the dried sludge were 68% and 25%, respectively **(Kongsricharoern and Polprasert, 1996)**

The operation cost of the ECP unit is found to be slightly lower than that of the conventional chemical precipitation processes.

### 4. Duckweed (Lemna gibba)

Duckweeds are a floating leaves macrophytes **(Sultan, 1999)**. These small floating plants have frond sizes between 2-20mm. They have high relative growth rate. They are characterized by their higher production and of valuable product rich in protein of 20-35% on dry weight basis. They grow very fast, need considerable amount of nutrients such as nitrogen and phosphorus. These characteristics make them look very suitable to be a base in a biological waste treatment system. Duckweeds are found in a number of species: Lemna gibba is one species.

Lemna gibba is one of the most resistant species to adverse conditions **(Sultan, 1999)**. It is found in waters of wide pH range. It has a life span of 29 days. It has high potential for wastewater treatment due to its ability to remove nutrients

Lemna gibba is capable to remove chromium efficiently from wastewater via adsorption mechanism.

### 5. Activated carbon

Activated carbon adsorption offers one of the most efficient processes available for removing certain organics and inorganics from wastewater. The capacity of activated carbon for a certain type of pollutant is important for designing adsorption-contacting systems **(McKay et. al, 1985)**. Among the pollutants removed by activated carbon are chromium ions.

## 2.7 Conclusion

The following conclusions can be drawn from the chapter:

- Different methods for removing and recycling chromium from tanneries are found in the literature. Each method has advantages and disadvantages.
- It has been found that wastewater by coagulation/precipitation is efficient and economic. Therefore, it will be the treatment method to be used for this study. The coagulant to be used in this study for the precipitation is the magnesium oxide. The quantities and method used will be detailed in the methodology chapter.

# Chapter Three

# Materials and Methods

# 3. INTRODUCTION

The following methodology was followed and used in this study:

(A) Collection of data: this covers the following points:

1. Visiting the existing Palestinian tanneries and distribution of a questionnaire
2. Sampling and lab analysis

(B)Literature Survey of treatment procedures used in tanning plants. (removal and recovery of chromium).

(C)Laboratory scale for removing Chromium from the effluent wastewater.

(D)Outline procedure for scaling up the process of the above step.

(E)The introduction of clean technology concept and carrying out this concept for an existing tannery

(F)Recommendations for building a main chromium treatment unit/s for the existing tanneries in Palestine

A more detailed description of each of the above is covered in the following sections

## 3.1 Qualitative and Quantitative Data Collection

1. Visiting the existing tanneries and distribution of a questionnaire

The visits were based in the following areas: Nablus, Hebron and Salfeet. Anabta tannery was not covered in this study since the advanced tanning processes are not done in this tannery. A questionnaire was distributed while visiting the tanneries. The questionnaire covers the following points: capacity of each tannery, number of working days, amount of water used, the possibility of existing treatment facility, existence of any safety precautions in the tannery for workers safety, and even investigating for the existence of any related disease in the area under study and any existing EIA that carried out before establishing tannery

A copy of the questionnaire can be seen in **appendix 6**.

2. Sampling and lab analysis for samples taken from the tanneries and particularly from intermediate stages of the tanning process

Experimental work:

Nine grap samples were taken from a single cowhide tannery during different processes. This is Palestine tannery in Hebron district. These nine samples represent six different processes, sometimes more than one sample was taken from the same process but from different batches. Another two samples were taken from the main manhole. There are two outlets running through the main manhole, each outlet is connected to a number of tanneries as well as to other industries. Therefore, the total samples taken was eleven.

Measurements of some parameters such as pH, conductivity, salinity, and total dissolved solids were performed directly after taking the samples (on site). Analysis was done using "Hach" pH meter and "Hach" conductivity meter **(appendix 7)**. A qualitative test was conducted for the sulfide for its presence using lead acetate paper and whenever this test result was positive, a sample was taken and preserved for later laboratory analysis.

Portions of the samples taken were placed in smaller containers and were preserved for later analysis in the laboratory. The preservation of samples was carried out according to the parameter that would be analyzed, and the preservation as well as the analytical methods were conducted according to the "standard methods for the examination of water and wastewater" **(APHA, 1992; appendix 3)**

Each analysis was conducted in triplicate and the average was taken each time. For the samples taken from different batches, 3 readings were taken from each batch sample and averaged, then the averages from different batches were averaged. Sometimes measurements for some parameters were not done if it is not applicable. Analysis was carried out in Birzeit University/Faculty of Engineering/Water Engineering Laboratory

## 3.2 Literature Survey of Treatment Procedures Used in Tanning Plants

This covers removal and recovery of chromium, chapter two of this study describes in details the different methods for the chromium removal, chromium recovery or/and both, with more emphasis on the method chosen in this study as the treatment method.

## 3.3 Laboratory Scale for Removing Chromium from the Effluent Wastewater.

Experimental work:

Three coagulants were used to examine the efficiency of chromium removal by coagulation precipitation technique. The three coagulants used are MgO, $Na_2CO_3$ and Prestol, (Prestol is a trade name and not a chemical name), it was obtained from Salfeet tannery. Its chemical formula is not known and according to the information taken from the tannery owner, it is a mixture of a number of chemicals. Experimental work was applied to real tanning liquors. The concentration of chromium in the tanning liquor as well as the pH were measured. A precalculated quantity of the first two precipitation reagents (in different doses) were added to a 100ml portions of samples of the liquor and stirred for two hours, after which the pH measurement, sludge volume and chromium content in the supernatant were taken and examined. The Prestol amount used was one teaspoon per one cubic meter of the tanning effluent as was suggested by the tannery owner. This will be equivalent to 10g, and so for the 100ml portion about 0.001g is to be used. As the lab balance has accuracy of 0.01g, therefore, a minimum amount of 0.01g was used.

In order to calculate the stoichiometric amount of chemicals used, the following chemical reactions were used:

A. $Cr_2(SO_4)_3 + 3MgO + 3H_2O \qquad 2Cr(OH)_3 + 3MgSO_4$

The by-weight stochiomatic value for Cr:MgO is [1:1.16](which means that 1.16g MgO coagulant is used for the precipitation of 1g Cr)

B. $Cr_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O \qquad 2Cr(OH)_3 + 3Na_2SO_4 + 3CO_2$

The by-weight stochiomatic value for Cr:$Na_2CO_3$ is [1:3.06](which means that 3.06g $Na_2CO_3$ coagulant is used for the precipitation of 1g Cr)

C. It is not easy to write the exact chemical equation for the reaction that takes place with Prestol since its chemical formula is not known

Analysis was then conducted to measure the efficiency of chromium removal by using the Atomic Absorption Spectrophotometer/Perkin Elmer brand **(Appendix 7)**

## 3.4 Outline Procedure for Scaling up the Chromium Removal.

Experimental work:

Among the above three mentioned coagulants, magnesium oxide was chosen as a precipitating agent. This experiment was conducted in Palestine tannery in Hebron, this is the same tannery from which sampling was carried out. The experiment was carried out on the effluent coming out from the tanning step, "step producing chromium", it was carried out on 200 L effluent sample. Initially, the concentration of chromium in the effluent was measured, then a calculated quantity of magnesium oxide sufficient for chromium precipitation was added to the 200 L effluent, which was previously screened in order to remove the suspended solids. Stirring was carried out by using a stick for at least one hour, pH reached 8 in this stage. The effluent was left for next day for the settling process after which decantation was done for the supernatant and the sludge formed was dissolved in the pickling water and sulfuric acid to reach pH of 2.5, then leather was tanned with this product. Samples were taken from the supernatant as well as from the remaining water of the tanned leather for lab analysis to estimate the chromium content

The following flow chart (figure 3.1) was conducted through the laboratory and pilot experimental work for the chromium removal and reuse

Results of the experimental work are shown in chapter 4

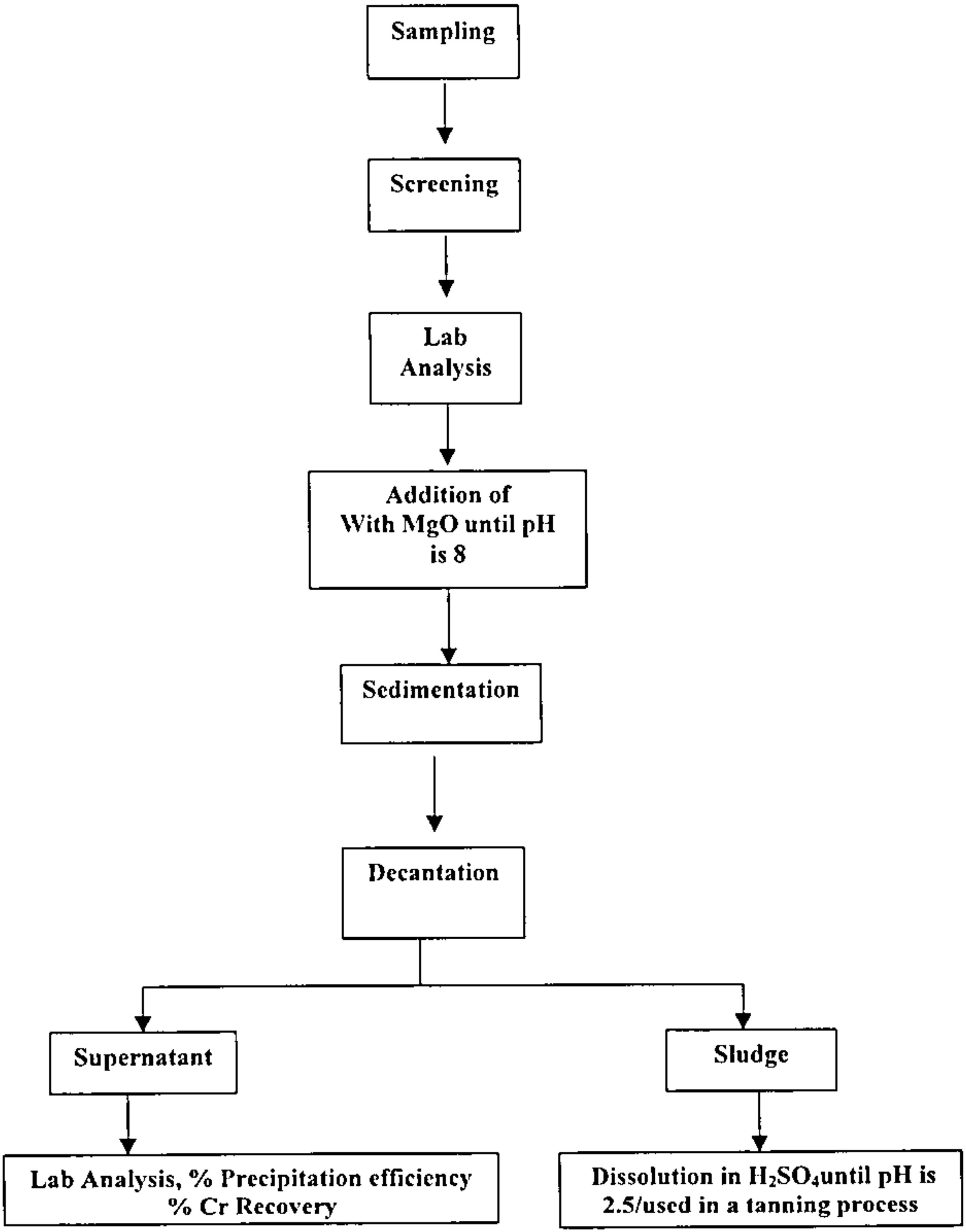

Fig.3.1 Experimental flow Chart for Chromium Removal

## 3.5 The Introduction of Clean Technology Concept and Carrying out this Concept for an Existing Tannery

This will be discussed in details in a separate part in this study "Clean technology" **(appendix 1)**

## 3.6 Recommendations for Building a Main Chromium Treatment Unit/s for the Existing Tanneries in Palestine

This will be discussed in details in the following chapter as well as in the last chapter of this study. The recommendations for building such a treatment unit/s will take into account the environmental considerations as the first priority, then the economics related to this will be the second.

# Chapter Four

# Results and Discussion

The following results are obtained to fulfil the objectives proposed at the beginning of the work

**4.1. Objective One:** To build a database of tanneries effluents characteristics (quantitatively and qualitatively).

To achieve this objective, two actions were carried out. The first was a distribution of a questionnaire in three tanneries in Palestine. The second was the sampling procedure and lab analysis from one of the tanneries covered in the questionnaire.

### 4.1.1. Questionnaire

#### A. Results

The information filled in the questionnaire (see Appendix 6) is summarized in Table 4.1

| | Data | 1-11 | 12, 13 | 14 |
|---|---|---|---|---|
| 1 | **Tanery location** | Industrial zone/Hebron | Industrial zone/Nablus | Industrial zone/Salfeet |
| 2 | **Number of employees** | 4-8 | 7 | 16-18 |
| 3 | **Production capacity** | 1600-2000 kg/day | 200 hide/day | 250-300 hide/day |
| 4 | **Flow sheet of the industrial process** | Not clear | Not clear | Not clear |
| 5 | **Evaluation of raw material and chemicals used** | Not clear | Not clear | Not clear |
| 6 | **Water consumption** | 15m$^3$/day | 10-16m$^3$/day | 10m$^3$/day |
| 7 | **Disposal of liquid wastes** | Municipal | Municipal | Tank |
| 8 | **Disposal of solid wastes** | Containers | Containers | Containers |
| 9 | **Existence of pollution control units** | No | No | Yes/not used |

**Table 4.1** Results of the questionnaire distributed in the tanneries

Notes

1. 1-11: eleven tanneries in Hebron(ten out of the eleven process cowhides)
2. 12, 13: two tanneries in Nablus
3. 14: one tannery in Salfeet

#### B. Discussion

Due to difficulties in reaching all the tanneries due to privacy, three tanneries were visited, one in Hebron, one in Nablus City and the third is a town nearby to

Nablus called Salfeet. The questionnaire was carried out in these three tanneries. Basic data about the other tanneries were generalized as they are located in the same area and have similar conditions.

When filling the questionnaire it was not easy to get some information from the tanners because they will consider it as privacy for their industry or because they are afraid from governmental actions related to environmental problems. Therefore, it was difficult to get the quantities of chemicals used in the tanning process or the procedure of the process itself. Also it was not possible to get information concerning any health troubles among the workers during their work from the tanners. So some information filled in the questionnaire and consequently in the above table are taken from tanneries owners and is not necessary be true.

### 4.1.2 Sampling and lab analysis

#### A. Experimental results

The results of the eleven grab samples that were taken from single tannery (represents the tanning of leather of cowhides) are reported in table 4.2.

| PROCESS | pH | COND ms | % SAL | TDS mg/L | TS mg/L | BOD mg/L |
|---|---|---|---|---|---|---|
| SOAKING (*) | 7.9 | 80.6 | 63.1 | O.R. | 75910 | 2502 |
| LIMING | 12.4 | 48.9 | 35.8 | O.R. | 59660 | 1193 |
| DELIMING | 9.27 | 24 | 16.3 | 15600 | 15745 | 2220 |
| PICKLING | 1.75 | 75.8 | 58.7 | O.R. | 65910 | 1713 |
| CHROME (**) | 2.6 | 66.3 | 50.5 | O.R. | 79090 | 1532 |
| SOAKING (*) | 8.23 | 53.2 | 39.3 | O.R. | 45950 | 2501 |
| VEG & OIL | 3.46 | 7.13 | 4.4 | 4330 | 23115 | 2269 |
| CHROME (**) | 2.69 | 61.5 | 46.3 | O.R. | 74540 | 1766 |
| CHROME (**) | 2.47 | 54.7 | 40.7 | O.R. | 65540 | 1735 |
| MANHOLE 1 | 5.14 | 19.2 | _ | 12500 | _ | _ |
| MANHOLE 2 | 9.02 | 17.88 | _ | 11200 | _ | _ |

**Table 4.2.** Results of eleven grab samples taken from a cowhides tannery.

| PROCESS | COD Mg/L | TKN mg/L | Cr mg/l | Grease & oil mg/L | Sulfide Mg/L |
|---|---|---|---|---|---|
| SOAKING (*) | 11330 | 378 | N/A | 805 | 10 |
| LIMING | 27900 | 2610 | N/A | 1310 | 2500 |
| DELIMING | 4620 | 2159 | N/A | 495 | 32.5 |
| PICKLING | 4810 | 599 | N/A | 815 | N/A |
| CHROME (**) | 8210 | 630 | 4135 | 85 | N/A |
| SOAKING (*) | _ | _ | N/A | _ | 7.5 |
| VEG & OIL | 32200 | 241 | N/A | 765 | N/A |
| CHROME (**) | _ | _ | 4260 | _ | N/A |
| CHROME (**) | _ | _ | 4405 | _ | N/A |
| MANHOLE 1 | 23650 | _ | 50 | 1245 | 106 |
| MANHOLE 2 | 5300 | _ | 70 | 690 | 113 |

**Table 4.2.** Results of eleven grab samples taken from a tannery processing cowhides (continued)

## Notes on the previous table

| | | |
|---|---|---|
| 1 | Field Analysis | pH, cond, %sal and TDS were done in the field |
| 2 | Manhole 1 & 2 | Taken or done for the typical untreated tanneries effluents |
| 3 | O.R. | Over Range:more than 20000 mg/L |
| 4 | N/A | Not Appliciable(expected to give negative results) |
| 5 | Soaking (*) | Soaking step but from two batches |
| 6 | Chrome (**) | Tanning step but from three batches |
| 7 | _ | Not measured at all |
| 8 | COND | Conductivity |
| 9 | %SAL | Percentage of Salinity |
| 10 | TDS | Total Dissolved Solids |
| 11 | TS | Total Solids |
| 12 | BOD | Biochemical Oxygen Demand |
| 13 | COD | Chemical Oxygen Demand |
| 14 | TKN | Total Kjeldahl Nitrogen |
| 15 | Cr | Chromium Content |

### B. Discussion

The parameters measured for the samples represent the common and most frequent tests that normally are done for samples from tanneries. Although the main interest of this study is to remove chromium pollutants from tanneries effluent, other pollutants were also characterized.

It is very important to remember that the tanning process is a batch one and involves the use of a large number of chemicals. This means that the characteristics of the effluents either combined or individual may differ from one sampling point to another, sampling time, batch to batch and other factors. The measured parameter values range vary from one tannery to another, and even in the same tanning batch as it is a function of the chemicals used, water consumed, time elapsed between the addition of chemicals and sampling time and of course type of hides under processing (cow, sheep or goat). Therefore, it is found in the literature that the effluent tanneries profile has a wide range. Table 4.3. Summarizes some of the expected results for the effluents

| Process | Type | TKN | COD | BOD | Oil & G | Cr | pH | Sulfide |
|---|---|---|---|---|---|---|---|---|
| **Soaking** | (a) | 623 | 4000 | 1800 | 500 | | 6.95 | 4.8 |
| | (b) | 428 | 5120 | 3000 | 200 | | 6.39 | 4 |
| | (c) | 1135 | 31050 | - | - | - | 7.7 | - |
| **Liming** | (a) | 2965 | 21500 | 9000 | - | | 11.94 | 2200 |
| | (b) | 452 | 14200 | 10000 | 900 | | 12.67 | 1320 |
| | (c) | 4040 | 58735 | - | - | - | 11.9 | 2670 |
| **Deliming** | (a) | 1238 | 790 | - | 50 | | 9.77 | 11.2 |
| | (b) | 1362 | 1920 | 600 | 20 | | 9.76 | 148 |
| | (c) | 3855 | 5235 | - | - | - | 8.6 | 134 |
| **Pickling/ Tanning** | (a) | 106 | 12000 | 4000 | - | | 3.11 | 24 |
| | (b) | 1182 | 3000 | 1000 | 200 | | 2.3 | 8 |
| | (c) | 670 | 2900 | - | - | 2530 | 3.6 | - |
| **Fat Liquoring** | (a) | - | 1600 | 1300 | 60 | | 3.76 | - |
| | (b) | - | 2320 | 1200 | 240 | | 3 | 4 |
| | (c) | 1068 | 4365 | - | - | - | 4.4 | - |

**Table 4.3.** Pollution profile of tanning process(all units are mg/L except pH)

Notes:

1. (a): Pollution profile of tanning processes of sheep hides **(Sengül and Gürel, 1993)**
2. (b): Pollution profile of tanning processes of goat hides **(Sengül and Gürel, 1993)**
3. (c): Pollution profile of tanning processes of cow hides **(Tünay et. al, 1994)**

To characterize the waste streams coming out of the different accompanied process, literature showed that tanning process is divided into subcategories. Table 4.4 lists the description of the subcategories and the wastes involved in each one.

| Subcategory | Processing | Waste Stream |
|---|---|---|
| I | Cattle hide processing from raw hide to chrome tanned finished product | Sulfide, Chrome, General |
| II | Cattle hide processing from raw hide to vegetable tanned finished product | Sulfide, General |
| III | Cattle hide processing from wet blue state to finished product | General |
| IV | Sheepskin processing from raw hide to finished product | Sulfide, Chrome, General |
| V | Sheepskin processing from pickled state to finished product | Chrome, General |
| VI | Sheepskin fur-suede | Chrome, General |

**Table 4.4.** Subcategories of leather processing **(Tünay et. al, 1995).**

In the following table, table 4.5. the expected quantitative composition of each subcategory effluent are listed. It is noticed that there is a wide composition range.

| Sub-category | COD | BOD | TSS | Sulfide | Cr | Reference |
|---|---|---|---|---|---|---|
| I | 4775-6400 | - | 1232-2993 | 59-158 | 367-1329 | **Kabdasli et. al, 1993** |
| I | 11145 | - | - | 278 | 76 | **Tünay et. al, 1994** |
| IV(sheep) | 4230 | 1500 | 3270 | 134 | 61 | **Sengül and Gürel, 1993** |
| IV(sheep) | 10380-26100 | - | - | 20 | 192 | **Kabdasli et. al, 1993** |
| IV(goat) | 3250 | 1844 | 6840 | 49.8 | 209 | **Sengül and Gürel, 1993** |
| IV(goat) | 8000 | 3900 | 1090 | 150 | 100 | **Talinli, 1994** |
| **Combined** | **5300** | **1920** | **2750** | **66** | **140** | **Tünay et. al, 1995** |

**Table 4.5.** Composition of the effluents of the subcategories of the tanning process. *(All units are in mg/l)*

As it can be seen, our experimental results, Table 4.1 are in agreement with Tables 4.3 and 4.5 .

**4.2. Objective Two:** To select, on the basis of literature data, the most suitable process by which chromium is removed and recycled from the tanneries effluent.

### A. Experimental results

The precipitation/coagulation was chosen and tested for the laboratory experimental work. In the experimental work, three coagulants were examined: magnesium oxide, sodium carbonate and Prestol. The results of the first two were compared as they functionally worked in the same way. Prestol was obtained from Salfeet Tannery and its chemical composition is unknown. Its chromium removal efficiency was done. For all the chemicals applied, different doses were used.

Based on the experimental results shown in Tables 4.6, 4.7, and 4.8 Magnesium oxide gave the best precipitation (removal) efficiency of chromium among the three chemicals for all doses used.

| | Dose | | |
|---|---|---|---|
| **Parameter** | **1:1** | **1:1.5** | **1:2** |
| **pH (final)** | 7.92 | 9.19 | 9.36 |
| **Sludge Volume (ml/L)** | 130 | 170 | 200 |
| **Cr(mg/l) content in the supernatant** | 0.29 | 0.4 | 0.42 |

**Table 4.6.** Results of precipitation using magnesium oxide

| | Dose | | |
|---|---|---|---|
| | **1:1** | **1:1.5** | **1:2** |
| **pH (final)** | 7.45 | 8.65 | 9.18 |
| **Sludge Volume (ml/L)** | 290 | 420 | 530 |
| **Cr(mg/l) content in The supernatant** | 2.05 | 5.05 | 6.9 |

**Table 4.7.** Results of precipitation using sodium carbonate

| | | | **Dose** | | |
|---|---|---|---|---|---|
| | **0.01g** | **0.1g** | **1.0g** | **5.0g** | **10.0g** |
| **pH (final)** | 2.81 | 2.87 | 3.35 | 4.36 | 4.87 |
| **Sludge Volume (ml/L** | No ppt | No ppt | No ppt | Gel | Gel |
| **Cr(mg/l) content in The supernatant** | as original | As original | as original | 43.38 | 39.56 |

**Table 4.8.** Results of precipitation using Prestol

**Notes on the previous three tables**

- Initial chromium concentration in the tanning liquor was initially measured to be 5,000mg/L.
- The volumes of tanning liquor used for experimental precipitation processes were 100ml
- The ratios used in the above tables are by-weight stoichiomatic values
- Initial pH was measured to be 2.50
- ppt: precipitation

### B. Discussion

By referring to the different effluent treatment methods discussed earlier in Chapter Two, the coagulation/precipitation method was used in this work. for the following reasons:

- The main goal of this study is to introduce the clean technology concept and to apply this concept in the tanning industry to remove a considerable source of pollution caused by chromium. Since the clean technology means achieving resource optimization, improving performance, reducing processing costs and overall reduction in the pollution load the coagulation treatment method satisfies this. Other methods used for chromium removal do not necessarily yield a reuse of the chemicals, at least through direct steps. Therefore, precipitation/coagulation method can be used for direct reuse of the chemicals with less number of steps. For environmental and economical reasons, any suitable methods should be able to remove and recycle chromium from the tanneries effluents. The precipitation/coagulation method does this. Chromium removal from the effluents and transferring it into sludge does not mean that there is no more danger, because finding a disposal method for the sludge containing chromium is not an easy and not cheap method. Also treatment by the precipitation of chromium proved to give the best removal efficiency.

From the coagulants used, Magnesium oxide was shown to give the best precipitating agent among the others used for the following reasons:

The idea of the addition of a precipitating agent to an effluent containing chromium is to convert the soluble chromium salts into non-soluble chromium salt (precipitate). In general, the most common precipitants are $MnSO_4$, $FeSO_4$, $FeCl_3$ and Alum. In terms of cost, these may compete with magnesium oxide, but the problem is in the nature of the precipitate produced. In such coagulants, the produced precipitate is different from the chromium salt normally used in the tanning process. On the other hand, the addition of magnesium oxide to the tanning liquor will raise the pH and precipitate chromium dissolved in the effluent as chromium hydroxide. According to the tanning process, just one step is needed before the reuse of this precipitate in a next tanning batch (dissolution of the precipitate with sulfuric acid which is part of the tanning process). This means that in case of using another coagulant, other chemical steps are still needed to convert the produced precipitate into the required chemical normally used in the tanning process

There are other precipitating agents working in the same mechanism of magnesium oxide (raising pH and precipitation as chromium hydroxide) such as sodium carbonate. Magnesium oxide is more preferable as it will yield less sludge volume and precipitate in less settling time. These parameters are important in the design of any suggested treatment plant

**4.3. Objective Three:** To introduce the clean technology concept and to apply it on the tanning industry.

The clean technology concept is discussed in details in a separate part in this study. It discusses the application of clean technology on the tanning industry, to all processes involved in this industry, beginning with leather as raw hides, passing by in between processing steps, until finished leather is produced.

## A. Results

The clean technology concept was applied experimentally on the tanning step, by which effluents containing chromium are produced

Chromium was recovered from the tanning process, then it was reused for the tanning of leather.

According to literature, 20-40% of the chrome used is discharged to the wastewater. According to the tanner, 8% chromium salt (chromium sulfate or chromium basic sulfate) is used, for a batch of 1500kg hide (which is equal to 100 hides), 120kg chromium salt is used. Therefore, 24-48 kg chromium is discharged into the wastewater. Experimental work for the reuse of chromium was carried out on 200L liquor.

The chromium content in the tanning liquor was analyzed by the atomic absorption spectrophotometer and it was about 5g Cr/L. Based on this, the quantity of chromium in 200L sample was calculated and it was 1000g Cr. The quantity of magnesium oxide, which was added, was also calculated and it was 1160g. pH reached about 8.

The supernatant was decanted next day by simple decantation and the precipitated $Cr(OH)_3$ was dissolved in 28L of the pickling water, "pickling is the step done previous to the tanning step and contains sulfuric acid, formic acid and salt". Additional sulfuric acid was added to reach a pH of 2.5, this pH is the one needed for the chromium salt to penetrate the inside of leather. Four hides were tanned by the produced chromium sulfate. The owner of the tannery in which this process was carried out reported that the quality of the leather tanned by reused chromium has the same quality of the leather produced by fresh chromium.

## B. Discussion

It is important to know the quantity of chromium present in the recycled tanning liquor in order to quantify properly the amount of magnesium oxide needed. It is also important to know the amount of sulfuric acid needed to dissolve the precipitated chromium salt before the tanning step. In general the precipitation of chromium is optimum at around pH 8 and the optimum pH for the tanning process is about pH 2.5.

These points are to be taken into considerations when establishing treatment plant for chromium.

It is valuable to note that the recovered form of chromium is either chromium sulfate ($Cr_2(SO_4)_3$) or basic chromium sulfate ($Cr(OH)SO_4$).

### 4.4. Objective Four: To determine the feasibility and efficiency of removing and recycling of chromium

Literature states that for a tanning plant with a capacity more than 1.7 $m^3$/day, it will be economical to remove chrome and recycle it. A case study: for a tannery that has a chrome recycling capacity of 12 $m^3$/day, the approximate costs are as follows:

Savings: 73,750 US$/year

Operating cost: 30,200 US$/year

Total net savings: 43,550 US$/year

Capital investment: 40,000US$

Payback: 11 months **(Cleaner Production Worldwide)**

So, the investment is so low that the payback period (calculated on the basis of chromium saved) is just 12-20 months. Money saved thus is money earned. Leathers obtained from recovered chrome are well accepted with international buyers **(Ramasami and Rajamani).** The owner of the tannery where the recovery experiment was carried out ensured this point.

# Chapter Five

# Conclusions,

# Recommendations

# &

# Future Work

## 5.1. Conclusions

Leather tanning industry in Palestine is still a traditional industry where the pollution load of this industry is high especially for chromium. Therefore, from what is carried out in the work, the following conclusions can be drawn:

1. There is a need for the application of treatment methods for the tanneries effluents in order to reduce the pollutants emitted from such effluents.
2. The clean technology is one of the means for reducing the pollution at the source.
3. The precipitation method was found to be the most appropriate method for chromium removal and reuse.
4. Magnesium oxide proved to be the best coagulant for chromium precipitation.

## 5.2. Recommendations

The following part will present some recommendations. More details can be found in appendix 2:

1. Awareness: it is important to improve awareness of both workers and owners of tanneries about the risks and environmental impacts of the tanning industry. This can be achieved through training of personnel.
2. Control and minimization of wastes: tanning industry produces both liquid and solid waste. These wastes are very harmful to the environment and should not be discharged as it is practiced today. Wastes should be treated before disposal. The best solution would be to minimize waste generation within tanneries by on-site recycling within the tanning process. This recycling can save resources for the tannery owners and can reduce the pollution coming out of the tanneries.
3. Control of gas emission: the tanning industry generates some toxic gases that can be harmful to the workers and the neighbors. One of the most dangerous gases associated with the tanning industry is the hydrogen sulfide which is mainly generated during the unhairing process. It is possible that high amounts of this toxic gas are present within drums or mixers and that it is distributed throughout the plant. Besides the fact that this gas is highly explosive, it has an unpleasant smell and may cause toxic effects like difficulties of breathing, headache and irritation of mucous membranes. To minimize the risks of gas emissions it would

be necessary to optimize the uses of the chemicals in the tanning industry, to provide efficient ventilation and to keep the plant clean.

4. Optimization of water consumption and the use of chemicals, diminishing discharge loads and providing a pretreatment.
5. Wastewater from tanneries should be handled separately and not discharged to the domestic sewage unless pretreatment is done.
6. As the tanneries are of small size (as the case in Hebron), they can share one pretreatment unit for their waste.
7. Tanners should be trained to do recycling on site to minimize discharge of liquid and solid wastes.

## 5.3. Future Work

Besides chromium, sulfur compounds are also very dangerous for the environment, and finding a proper treatment method for sulfur compounds is also urgent and needs a systematic study in which special concern is needed. Another important matter that needs great attention is the huge quantities of water consumed in this industry and the application of methods for water conservation is very important.

In the following part, a brief discussion of the environmental impacts due to sulfur compounds is mentioned, in order to draw some attention to this problem. Also the water conservation methods is to be discussed.

Sulfur compounds used in the tannery process are sulfides such as sodium sulfide ($Na_2S$), and sulfates as ammonium ($(NH_4)_2SO_4$) and as chromium sulfate ($Cr_2(SO_4)_3$). Because the uptake of the chemicals is never complete in the technological process, these compounds form part of the pollution in the effluent.

Sulfides cause a series of environmental problems: toxicity (the $H_2S$ threaten the lives of numerous workers in sewers); corrosion of concrete walls of reactors, steel pipelines; nuisance odour and oxygen demand.

Sulfates, at standard conditions, are not offensive for the environment, not toxic, do not demand oxygen in the water solution and are very stable chemically. However, in anaerobic conditions sulfates are reduced to sulfides generating problems described above. Moreover, in anaerobic treatment systems, the presence of sulfates hampers the anaerobic digestion.

The maximum allowable limit for sulfides coming from the tanning leather industry is 0.1 mg/l. However, the expected average concentration of sulfides in the tannery combined effluent is in the range of 350 - 500 mg/l with variations between 1500-2900 mg/l in the effluent of the unhairing process. The extremely high concentration of sulfides in the effluent of the unhairing process causes an unpleasant smell, danger to people because of intoxication, a high oxygen demand, and corrosion of equipment and concrete canals in the enterprise.

Although the concentration of sulfates in the tannery effluent is also high, this sulfur compound represents just a potential environmental problem: when the conditions remain aerobic no $H_2S$ release occurs.

**Considerations of impact on the environment by sulfur compounds**

Among the numerous environmental problems that the tanneries have to confront in the future, the contamination by sulfur compounds is becoming one of the most serious problems.

Sulfur compounds appear in the tannery effluent from the various stages of the tanning processes: from the unhairing process where lime blended with sodium sulfide is traditionally used to dissolve the hair into a pulp; from the deliming process as ammonium sulfate and as chromium sulfate from the tanning step. It should be noted that around 30-40 per cent of chromium sulfate used in the tanning step is not retained by hides but ends up in the wastewater creating a high concentration of sulfates. In anaerobic sections of sewers and canals as well as in anaerobic treatment systems part of sulfur compounds are reduced to sulfides, which causes numerous problems such as:

- Toxicity: With cyanide gases and phosgene, hydrogen sulfide is one of the most toxic gases. At high hydrogen sulfide concentration (500 - 1000 ppm), it acts primarily as a systemic poison, causing unconsciousness and death through respiratory paralysis. In lower concentrations (50 - 500 ppm) $H_2S$ provoke a respiratory irritation.

- Corrosion: $H_2S$ may cause damage to concrete walls of reactors, sewer system and steel pipelines as well.

- Odour: Hydrogen sulfide has a very characteristic rotten eggs odour which is perceptible in fresh air in a concentration of 0.2 ppm.

- Oxygen demand: Sulfides present in the wastewater need a substantial additional amount of oxygen to be oxidized. Theoretically 2 mg COD per mg sulfide is required to form sulfate.

In addition, a potential problem related to the presence of sulfide in wastewater is a poorly settling sludge.

**Water conservation**

Water conservation has important secondary benefits, in addition to reducing demand on the water supply. Lower water consumption implies smaller sized plants (especially treatment plants), reduced consumption of chemicals, and likely lower operating costs, including the cost of energy. However a reduction in water will not reduce the pollution load if the same wasted material is merely concentrated in a smaller volume.

Variations in water consumption range from less than 25 l/kg of raw hide to greater than 80 l/kg for apparently similar technologies. A working figure of 50 l/kg is generally accepted. There is often considerable scope for improvement in efficiency of water use through:

1. Increasing volume control of processing waters;
2. "Batch" versus "running water" washes;
3. Low float modification of existing equipment;

4. Low float techniques using updated equipment;
5. Reuse of wastewaters in less critical processes;
6. Recycling of individual process liquors.

Finally there is an important need to set strategies for pollution control caused by the tanning industry sector **(Chernicharo and Van Vliet, 1996)**. The plan of work for pollution control in the tanneries comprises three phases

1. **Diagnosis of the industrial sector**
    i. Location of each tannery
    ii. Number of employees
    iii. Installed and actual capacity of production
    iv. Flow sheet of the industrial process
    v. Evaluation of raw material and chemicals used
    vi. Water and energy consumption
    vii. Disposal of liquid and solid wastes
    viii. Existence of pollution control units
    ix. Availability of area for treatment plant
    x. Local environmental impacts

2. **Training of human resources**

Courses on pollution control in tanneries, treatment of tannery effluents, environmental technologies applied to tanneries

3. **Technological development**
    i. Improvements in the industrial process
    - Change and reduction of the chemicals
    - Effluent segregation
    - Use of cleaner technologies
    - New and better equipment
    - Recycling and reuse
    - Education and training

ii. Treatment of liquid effluents

Combination of physical, physical-chemical and biological units and processes

- Chrome precipitation
- Sulfide oxidation
- Other pollutants removal

iii. Solid waste

iv. Atmospheric emissions

Hydrogen sulfide

The scope of the future work is beyond the work under investigation. Therefore, it is recommended that the future work mentioned above to be carried out by successor researcher in collaboration with the national environmental authority in order to achieve a green environment.

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# Appendix One

## Clean Technology

# A1 INTRODUCTION

Environmental management, over the past years, has focused on the end-of-pipe waste treatment, design of waste treatment plants and installation of pollution abatement equipment for preventing/abating industrial pollution.

However, recent years have seen a progressive shift from waste treatment to in-house modifications. These modifications are mostly in the "process stream design" for achieving resource optimization, improving performance, reducing processing costs and overall reduction in the pollution load. These in-house modifications are commonly known as "Clean Technologies". Such technologies involve the continuous application of an integrated preventive environmental strategy to processes and products so as to reduce risks to humans and the environment. These result in conservation of raw materials and energy, elimination of toxic raw materials, and reduction in the quantity and toxicity of all emissions and wastes before they leave a process. Cleaner production serves the dual function of avoiding waste generation on the one hand, and minimizing the use of raw materials and energy on the other **(PTA/LIDO, 1995)**. Naturally the combination of cleaner production processes and reduction of water consumption, together with treatment of residuals, will be the most effective solution **(UNEP IE/PAC, 1991)**.

Many options are available for improving production technologies in order to increase environmental performance. Improvements can have a number of objectives, such as:

1. Increasing the efficiency of chemicals utilization;
2. Reducing water and energy consumption;
3. Recovering or recycling rejected materials

These objectives are often linked, and achieving one may automatically entail the achievement of the others as well. Of course these technical considerations are additional to those pertaining to the type of the product and the most economic way to produce it **(UNEP IE/PAC, 1991)**.

# A1.1 Specific Tanning Processes: Environmental Impacts and Clean Technology Options

## A1.1.1 Preservation (salt curing)

### A1.1.1.a Environmental impacts:

The main environmental issue of the preservation of raw hides and skins is the use of salt (sodium chloride) as a preservant. High concentrations of chloride in the effluent of the curing plants and in the first steps of the beam house operation cause high salinity of natural water bodies, which has to be avoided, since there is no economic way of removing salt from effluent **(PTA/LIDO, 1995)**.

### A1.1.1.b Clean technology options

It is recommended that the following procedures need to replace the conventional salt preservation process:

1. Processing of Fresh hides and Skins

Processing of fresh hides and skins is the best alternative from the point or view of the chloride load of the effluent. No use of any chemicals and bactericide results in a better quality effluent. Soaking process can be replaced by washing procedure. Fleshing is possible just before the liming-unhairing processes, hence results in reduction of the quantity of chemicals. Fleshing by product will be of better quality. However, time elapsing between slaughtering and further treatment (e.g. beam house processing) must not exceed a few hours, mainly when the temperature of air is high to avoid putrefaction **(PTA/LIDO, 1995)**.

2. Air Drying

This is one of the oldest methods of skin preservation. It is the standard method of preservation of most reptile, goat, and fur skin and of a very large percentage of the hides and skins obtained in the tropical areas.

This technique is a simplest form of preservation; most practical in areas where salt is expensive and a small number of skins are to be cured; particularly useful in dry, tropical climates and in rural areas of some under developed nations. However, some of the disadvantages of this technique are also very important and described here. The rate of drying is of great importance. If it is too slow, putrefaction may begin in the hide before the moisture level can be decreased to the point where bacteria can no longer be active. If drying is too fast, the outer surfaces of the hide may become hard and dry while the inner parts still have enough moisture to support bacterial growth. This " case hardening " of the hides may rot out from inside. Upon soaking for processing, the hide will have a blistered appearance and eventually holes will appear. Skin may get damaged from the permanent fold marks of hanging, and direct sunlight may cause case hardening of the upper surface. In case of spreading on ground, supported on sticks or stones, it will be necessary to prevent the skin to be damaged by insects.

As many difficulties are associated with this technique and common salt is also not expensive in Palestine, therefore, to replace the salt curing with this curing technique looks unjustified and impractical **(PTA/LIDO, 1995)**.

3. Chilling of Raw Hides and Skins

This process permits the long preservation time as compared to the processing of raw hides and skins depending upon the temperature applied, which can last up to three weeks without problem.

The most substantial question concerning chilling preservation is the time between flaying and the freezing of the hides. It has to be as short as possible.

Each piece has to be frozen separately to assure that a fast cooling can be reached before putrefying processes begin to damage the hide tissue.

Chilling is done with shredded ice, cold water and cold air.

i. Chilling with ice requires about 5kg ice to chill one hide. It is spread on the flesh side of each hide piled inside a box. The raw hides can be sent to the tanneries, while a temperature not higher than 8°C has to be maintained for a maximum of three weeks.

ii. Chilling with cold water requires cold water spray or batch to reduce the hides' temperature rapidly just after flaying, and thus, facilities further refrigeration by other systems.

iii. Chilling with cold air is carried out in a refrigerated store. Each hide has to be hung and stretched, without coming into contact with others, to permit the freezing of the entire surface. By keeping the temperature between -2°C and +5°C, the hides can be stored up to 3 or 4 weeks without any other auxiliary agent.

Some of the disadvantages include, energy consumption, necessity of freezing equipment and cold storage. Additional efforts to maintain equipment and installations and to control the operation are required **(PTA/LIDO, 1995)**.

### 4. Hide Preservation Using Bactericides

At present, bactericides can be used for short time preservation only. As bactericides have severe ecological impacts if released to nature (water, soil, food, and food chains), the use has to be controlled effectively.

For the selection of biocides, the following points should have to be taken into consideration:

a) If there is a choice of more than one product, less toxicity and high biodegradability should be the criteria for the selection of one.

b) Instructions for the use of bactericides have to be followed strictly.

c) Personnel using biocides have to be trained, and safety equipment should be used effectively

This technique can only be environmental friendly if the above mentioned precautions are adopted strictly **(PTA/LIDO, 1995)**.

### 5. Salt Recovery and Minimization

Salt curing still remains the mostly widely used method for preservation of hides and skins. Although not considered a clean technology, and despite intensive research work, no alternative process of comparable economic and ecological efficiency could be found. Due to low cost, easy application and long-term effect, it seems that salt preservation will be used worldwide for the years to come **(PTA/LIDO, 1995)**.

However, the adoption of cleaner technologies for recovery and minimization of salt concentration in the soaking effluent is possible. Options available include:

A. To pre-flesh the hides before salt application to reduce the weight and consequently the amount of salt to be used.

In pre-fleshing, it will be necessary to bring the raw hides/skins in the tannery as soon as possible after flaying from the slaughterhouse. Otherwise, putrefaction of hides/skins may occur due to the high temperature and humid climate. The same problems as processing of fresh hides and skins are also associated with this technique.

B. To shake the salted hides in a sieve drum or a similar device, or manually prior to the soaking process, to take off part of the salt adhered on the hides' surface. The recovered salt can be returned to the curing process again.

C. Introducing a washing step prior to the soaking step after the removal of adhered salt as described above. The washing should be carried out with little quantity of water. This washing will dissolve most of the salt from the hides and skins. The effluent resulting from this washing step may be collected and subjected for sun drying in open dishes. After water evaporation, salt can be reused for curing purpose.

## A1.1.2 Soaking

### A1.1.2.a Environmental impacts:

The environmental impact of the soaking process depends to great extent on the characteristics of the processed raw hides and skins, fresh, salted, or preserved by any other method. Moreover, the use of surfactants, bactericide, alkali and sulfide in the process are the important contributing factors along with the load of solids and soluble proteins which are washed out of the hides during the concomitant cleaning procedure **(PTA/LIDO, 1995)**.

### A1.1.2.b Clean technology options

Enzymatic products are considered to be less toxic and can be a good replacement of sulfide. Surfactants, if used, should be selected with respect to their biodegradability. Alcohol ethoxylate based products are preferable.

If bactericide is used, properties like less toxicity and high biodegradability should be considered. Most of these products are more expensive than traditionally used PCP and may not have the same long-lasting effect.

If hides are not pre-fleshed neither in the slaughterhouse nor in the preservation plant, green fleshing work just after deep soaking is a suitable procedure to obtain a by-product at pH close to neutral, which can then easily be processed to recover fats and proteins with good marketing possibilities and to save liming-unhairing chemicals.

The use of pits or paddles for soaking operations results in a higher consumption of water, mainly for the washing phase which are much less efficient than when using drums. Even for drums, it can be recommended to operate with sequential washing instead of continuous rinsing which leads to the saving of enormous amount of water at this stage.

To reduce the volume of effluent, possibilities should be investigated to perform soaking and unhairing in a single stage. This approach could reduce the volume of effluent for this stage to 4-5 L/kg raw hide. Although such savings do not directly reduce the pollution, however, they can lead to reduction in the water consumption in a tannery and reduction in the size of the effluent treatment plants **(PTA/LIDO, 1995)**.

## A1.1.3 Unhairing and Liming

### A1.1.3.a Environmental impacts:

The unhairing-liming process only consumes 40 to 45 % of lime and 50 to 55 % of sodium sulfide or sodium hydrosulfide in the treatment float.

Unhairing and liming process is responsible for 55 % of COD, 70 % $BOD_5$, 40 % of nitrogen and 76 % of the toxicity in tannery effluent. In addition to this, a large amount of settleable matter also comes from this process in the effluent. Hair destructing system produces 122 %, 58 %, and 157 %, more suspended solids, $BOD_5$, and COD respectively as compared to the hair saving system. There has been continuing research to find new technologies to avoid this large pollution load **(UNEP IE/PAC, 1991)**.

Sodium sulfide and sodium sulfhydrate used for unhairing process are most dangerous materials. Upon acidification, solution containing sulfides, even in trace amounts, will release hydrogen sulfide gas into the atmosphere. The gas is heavier than air and may accumulate in sewers or wherever solutions from acid processes and sulfide unhairing system come together. Hydrogen sulfide at very low levels, has a noxious odor and at high enough levels it could be fatal, paralyzing the nerves, and fatality may result without warning **(PTA/LIDO, 1995)**.

### A1.1.3.b Clean technology options

There are two major possibilities for improvement in the unhairing process; these are:

- Pollution Reduction in Conventional Methods; and
- Use of Alternative Methods **(PTA/LIDO, 1995)**.

1. Pollution Reduction in Conventional Lime Sulfide Method

i. **Hair Saving Methods**

Hair saving systems use smaller quantities of sulfide as compared to hair destruction system, and allow an easy separation of the proteins constituted by the undissolved hair and hence imply less pollution than the hair destruction process. In this process, the hair is loosened and removed from the hides but not pulped or dissolved in the float. The installation of a screen is required to remove the hair from the unhairing liquor. The procedure results in a significant reduction of COD, BOD, nitrogen, sulfide, total and suspended solids in the wastewater, besides a decrease of sulfide consumption. Hair recovered through this process can be reused, at least, as nitrogen source in agriculture, or for making brushes, mats, ropes, and felt production.

### ii. Recycling of liming Liquor

Some of the liming unhairing techniques permit a direct reuse of the spent liquors after decantation and / or filtration to separate the sludge containing lime, fat, and proteins, and then recharging with chemicals according to the recipes. The number of recycling steps depends on the efficiency of the clean-up process for the spent liming liquor, and on the desired leather quality. The liquor may be regenerated and reused many times, which may even be up to 30 times. The procedure permits saving of water, sulfide and lime. The sludge recovered through this process may be used in agriculture. Only the pH of the soil and the application dose have to be considered.

### iii. 2.1.3.b Recycling of Unhairing liquors

For several years, experiments and practical processes have been performed to re-use unhairing liquors after separation of insoluble substances by sedimentation. Important savings are claimed.

A second consequence of the high degree of pollution of the wastewater is that more water is needed to wash the unhaired hide. Another drawback is that the hair proteins are strongly destructed, because the proteins are exposed to the sulfide for a very long time.

### iv. TNO Proteins Separation Method

The main pollutant in beam house effluent is dissolved proteinous material. The minimum solubility of proteins is found at pH value between 3 and 4. Low solubility at pH 3 and 4 is the basis of the TNO method. However, before the pH can be lowered, the sulfide in the unhairing liquor must be removed, to avoid the development of gaseous hydrogen sulfide. This is done by the aeration of the liquid in the presence of divalent manganese (50g $Mn/M^3$). Soaking, unhairing and eventual deliming liquors are collected in the wastewater pit. After addition of manganous sulfate, the mixture is kept homogeneous by means of the circulation pumps and is aerated for some hours. After complete oxidation, bicarbonate (1 kg $NaHCO_3$) is added. Subsequently, the aerated mixture is introduced into the protein separator and a measured amount (10-20 L/M$^3$ wastewater) of concentrated hydrochloric acid is added through the different injection points to obtain an end pH of 3.5. After this, several pulses of compressed air are injected to get a smooth floatation of the insoluble proteins within half an hour. After removal of the clear liquid, under the proteins layer, a fresh quantity of wastewater can be introduced and the earlier procedure, described before, may be repeated. After some 5 or 6 charges and removal of the clear liquid, the protein cake can be driven out, using the screw. In case of optimum unhairing processes, about 80 % of the organic pollution present can be separated as a liftable sludge, with a composition of water (80 %), proteins (12 %), fat (4 %), and salt (4 %).

Amino acid composition of the protein-fraction of the sludge is comparable to that of the feather meal. In case of working with fresh hides of known origin, this sludge may represent a valuable additive to animal fodder. In case of salted hides of less known origin, the likely presence of preservatives may only leave open their application as fertilizer.

### v. TNO Unhairing Method for Destruction of Proteins during Unhairing

Long unhairing time and high sulfide concentrations contribute to higher solubility of the proteins formed. Moreover, the sludge formed in these cases after acidification becomes much less coarse and more strongly hydrated. For this reason, these sludges are much more voluminous and have a worse filterability. To improve protein separation, unhairing procedures were worked out in which the process is split up into a 2-7 hours lasting unhairing phase and a liming phase which may last 5-40 hours or even longer. In this way any opening of the hide structure by the lime can be realized, while the hair destruction is always very moderate, so that the protein separation can take place very efficiently. As the lime liquor is hardly polluted, it can be re-used several times in the liming process or recycled through the unhairing process.

### vi. Sulfide Oxidation

A separate pre-treatment of the toxic sulfide salt and organic sulfide compounds formed during liming-unhairing is the oxidation to non-toxic sulfate. Further, this procedure helps to avoid the formation of toxic and smelly hydrogen sulfide gas, and contributes to a higher and better economy of the final effluent treatment.

### 2. Alternative Unhairing Methods

Quite a lot of research is going on to find satisfactory alternative to the use of sulfide or to minimize its quantity for unhairing purposes

### i. Dimethylamine Sodium Hydroxide System

"This method is proposed by the Rohm & Hass Chemicals Company"

Dimethylamine has long been known as an effective unhairing agent when used in the lime systems. The proper maintenance of a balance of caustic soda in the system is of great importance. As a result of this work, a 24 hours hair saving procedure employing dimethylamine sulfate (DAMS) and caustic soda has been used on calf skins and cattle hides to make both light weight leathers and heavy sole leathers. One of the main drawbacks of the system is that the stock is quite slippery due to caustic soda, which makes it more difficult to handle. In the interest of economy, and also to decrease the strong action of the caustic soda, the system has been modified to incorporate DAMS, lime, soda ash, and sodium sulfhydrate. By using a balance of these materials, the harshness of the caustic soda is overcome by a buffering action attributed to the lime

### ii. Oxidative System

"This method is introduced by Germany, the unhairing is done by strong oxidizing medium and under acid conditions"

The active ingredient in oxidative unhairing is chlorine dioxide which reacts with the sulfur-sulfur bonds of keratin to produce a keratin sulfonic acid and free chlorine. The keratin substance of the epidermis is then converted into water soluble materials, and in the weekly acid medium the hair and the epidermis are removed by the mechanical action of the drum itself. The chlorine liberated from the reaction is absorbed by the collagen. It is claimed that large quantity of the natural fat is saponified and a loosening of the fiber structure of the hides is achieved so that the unhaired hides can be pickled and made ready for tanning operation, in about twenty four hours. The medium used is glycol acid, which maintains a buffered pH value between 3 and 3.5. In order to maintain the proper pH value, sulfuric acid is added. The temperature is maintained below 40°C in order to prevent any hydrolytic decomposition of the collagen, and slowly rotating drums (4-6 rpm) are used to prevent the generation of the heat. The strong oxidizing action of the chlorine dioxide and chlorine results in the bleaching of the hair, and there is no dark scud left on the hide. After completion of the unhairing, the excess oxidizing agent is decomposed with thiosulfate in order to prevent the strong oxidizing agent from being carried over into the chrome-tanning bath. The strongly oxidizing chlorine dioxide would oxidize the trivalent chromium tanning agents into dichromate. It is also claimed that the absorption of the chlorine by the hide proteins has the advantage of giving a fine grain and making a somewhat firm leather. The excess oxidizing agent must be reduced with thiosulfate prior to the use of vegetable tanning, in order to avoid excessively rapid fixation of vegetable tanning agents. Chrome tanning can, however, be conducted in the usual manner

The oxidative system has drawbacks in the high cost of materials and the necessity of shifting production from an alkaline system to an acidic system, which would mean a complete readjustment of the subsequent process of tanning, coloring, and fat-liquoring etc.

### iii. Enzymatic Unhairing

Enzymatic unhairing may be considered to be one of the newest and yet of the oldest practical methods. A wide variety of the enzymes can be used for this purpose. However, a keratin selective enzyme that does not attack collagen has yet to be found for the use on commercial scale. There are different ways to carry out unhairing with enzyme, as described below

- Sweating Process

This system is applied by dipping the skins in water and hanging them in a moist room for a period of time until the hair slip took place by natural wild bacterial growth. The system is resulted in a clean unhairing system, but if the skins are left too long, more often excessive damage to the hide collagen resulted and pits and holes are found in the leather. Therefore, higher levels of skills are required to handle the sweating process

- Enzymatic Unhairing at neutral pH

This system produces very tight leather. Due to the absence of swelling of the collagen, during tanning through conventional procedure; fine grained, tight leather with a tendency to be tinny, hard and thin is produced. Extensive modifications of the subsequent tanning, coloring and fat liquoring procedure are necessary to compensate for these drawbacks. The simplest way of correcting the disadvantages is to introduce an alkaline swelling bath of either lime or caustic soda prior to the pickling and tanning operation

- Enzymatic Unhairing in combination with Lime and Sulfide

The cost of the enzyme has been a drawback in some instances. In a low cost enzymatic unhairing, a mixture of sodium sulfide, sodium bisulfite, and ammonium hydroxide, a buffered medium at a pH of 9.5-10 was obtained in the presence of strong oxidizing agents. The enzyme, papain, introduced into this system exhibited very strong unhairing action. Excellent unhairing results were obtained, but it was necessary to modify the tanning process by intermediate alkaline treatment, and also to modify subsequent tanning process

### iv. Molescal System

"This system has been developed by the BASF cooperation"

This is a Proprietary Product which has the property of being an active sharpening agent, at the same time, it is easily oxidizable and very little sulfide remains in the system. The Molescal System can be used with or without the addition of a small quantity of sulfide to aid in the unhairing and can be used for both hair destruction (burning) and hair save leathers. This greatly reduces the sulfide effluent which is attractive to tanners, particularly with effluent problems. The leather quality is equivalent to that from a lime sulfide unhairing system

### v. **Lime Splitting and Trimming**

Lime splitting and trimming is usually carried out after tanning which results in by-products of low quality containing chromium in it. If these procedures are carried out with the pelt, the produced by-products can be sold easier in the market than those resulting from splitting and trimming of wet-blue (tanned hides). This will result in a reduction in the quantities of chemicals used for deliming, pickling, tanning, and consequently the load of the pollutants in wastewater after the lime splitting to get a uniform opening-up of the hides. To conduct the lime splitting successfully, tanneries have to train the beam house workers well to perform proper work under lime conditions, and correct adjustment of the split machine is necessary. The non-tanned by-product will be a good raw material for the manufacturing of gelatin or animal feed stuff.

## A1.1.4 Deliming and Bating

### A1.1.4.a Environmental impacts

The deliming phase using ammonium salts, bring about considerable nitrogen pollution, estimated to be as much as 40 % of the total discharge. Moreover, there is a risk of formation of toxic hydrogen sulfide gas during this process **(PTA/LIDO, 1995)**.

### A1.1.4.b Clean technology options

1. Oxidation of Sulfide

To avoid the formation of hydrogen sulfide during the acidification of the deliming floats, the oxidation of the sulfide present in the liquor by using hydrogen peroxide or sodium hydrogen sulfite is required.

2. $CO_2$ Deliming

The use of carbon dioxide seems to provide quite a few advantages as far as pollution is concerned. In practice, the only difficulty is related to the required distribution equipment of $CO_2$ from storage. This technology avoids the use of nitrogen salts. Furthermore, it helps to avoid an increase of the COD value cause by the use of organic acids. From technical point of view, the results obtained are very favorable for light pelts (thickness lower than 3 mm). The $CO_2$ is injected directly in the axle of the drum. The application rate is 1 to 1.5 % of the weight of pelts. For thicker hides, diffusion remains rather slow and requires much greater $CO_2$ amount, and it is necessary to increase float temperature (up to 35°C) and/or process duration, and/or to add small amount of deliming auxiliaries. A large amount of $H_2S$ appears at the beginning of the reaction requiring pretreatment with hydrogen peroxide

Since the pH of $CO_2$ deliming float is lower than that used in the common procedure, special ammonium free bates should be used

Currently, more than 100 European and American firms are using this technology, and the advantages of the process should ensure its rapid development. The cost of chemicals is slightly higher than those used in the conventional scheme

3. Weak acid (Organic) Deliming

It is useful to mention the use of the weak acid in deliming operations (lactic acid, acetic acid, etc.) but their cost limits their application to specific cases. The cost is 50 to 100 % greater than the conventional scheme, although the application rate is not more than 0.5 to 1 % of the pelt weight

## A1.1.5 Degreasing

### A1.1.5.a Environmental impacts

Oil and grease affect the receiving water by limiting oxygen transfer and thus reduces dissolved oxygen levels, which in turn may also affect the gills of the fish and plumage of waterfowl. Emulsified oil which settles on the bottom of water courses has the same effects as other suspended solids

The degreasing agents commonly in use are organic solvents, which release a greasy residue after recovery. Parts of the solvents may be emitted as vapor to the air during the process

Surfactants, if used instead of solvents, leads to a higher value of COD and BOD in the effluent because of the presence of dissolved greases and surfactants in the stream **(PTA/LIDO, 1995)**.

### A1.1.5.b Clean technology options

1. Recycling of Degreasing Solvent

Adequate equipment for storage, recovery and regeneration of solvent has to be provided to permit the correct handling of solvents and to avoid their release to the environment. If the extract brines are recycled, grease is recuperated, solvent vapors are controlled, and the occupational exposure is minimized. Such a system may be considered as environmentally sound, depending on the available technical possibilities. However, investment costs for the implementation and operation are higher than those for the methods using surfactants. Furthermore, it is imperative to avoid solvents containing halogenated hydrocarbons

In recycling procedures, the degreasing float and the three extraction pickling brines have to be collected in a vertical tank. Three phases are obtained

i. A salty aqueous phase, which is perfectly reusable for a new extraction. The sodium chloride solution reaches 90 % of its initial concentration. The required concentrations of water and sodium chloride are adjusted before recycling

ii. An organic phase, rich in solvents and combined fat solvents, which may be regenerated through stream-stripping

iii. An intermediate emulsifying phase, which can be controlled by using little emulsifier and bringing the temperature of that phase to 50°C

All in all, 50 to 70 % of the solvent may be recovered, and distillation residues may occasionally be upgraded. This upgrading may only take place if large volumes are involved. Residues such as tallow mat then be upgraded **(PTA/LIDO, 1995)**.

2. Degreasing with Surfactants

This procedure contributes water pollution (COD, BOD). Many suppliers offer products based on alcohol ethoxylate, which are considered to be more biodegradable than the traditional nonylphenol ethoxylate based products, and therefore they should be preferred **(PTA/LIDO, 1995)**.

## A1.1.6 Pickling

### A1.1.6.a Environmental impacts

Spent pickling float contains very high amount of chloride due to the use of salt as non-swelling agent. Residues of the fungicides, if applied, will also be present in the pickling streams. Pickling is usually carried out with the tanning. Therefore, environmental impact is usually seen with respect to both processes. However, if pickling and tanning processes are performed in separate float, a pickling effluent will arise from the beam house operation. The same environmental impacts that lead to a lowering of the quantity of salts during soaking process are associated with the pickling process **(PTA/LIDO, 1995)**.

### A1.1.6.b Clean technology options

1. Recycling of Pickling Floats

Today, recycling of pickling flats is a common practice in many tanneries of the world to reduce the salt pollution. After collection, the used float is sieved and its acidity (mainly from formic and sulfuric acids) is controlled by laboratory test. After readjustment to initial pH value, the float is reused for the following cycle. In practice, salt savings are about 80 % and reduction in acid consumption is estimated to be 25 % **(PTA/LIDO, 1995)**.

## A1.1.7 Tanning

## A1.1.7.1 Chrome Tanning

### A1.1.7.1.a Environmental impacts

The principal environmental concern of the tanning techniques originates mainly from the excess of the tanning agents. Significant quantities of the offered chemicals are not fixed in the collagen, and thus, either remain in the spent float and are squeezed off during the sammying operation or are washed out by the wet finishing float. Another part of the offered tanning agents is washed within the solid residue produced by some mechanical works which are performed after tanning (shaving, trimming, buffing)

As in "one bath tanning" method, basic chromium sulfate is applied in an acid medium under which conditions only trivalent chrome ($Cr^{+3}$) can be released. This is much less toxic than hexavalent chrome ($Cr^{+6}$) which is toxic to bacteria at a concentration of 2 mg/l. Hexavalent chrome will only enter in tannery effluent streams following spillage or incomplete reduction of hexavalent in tanneries which prepare their own tanning solutions (two bath method). For humans, hexavalent chromium or chromate is extremely hazardous inducing lung cancer, tumors and kidney inflammation at very low concentrations

Besides the environmental factors there is also an economical loss due to the drainage of unused chromium salts in the effluent, which is almost 25-30 % of total chromium applied during the tanning process

In case of the bleaching process in the tannery, the generation of sulfur oxide gases creates hazards for the workers by affecting their eyes and respiratory track **(PTA/LIDO, 1995)**.

### A1.1.7.1.b Clean technology options

Most chrome tanning technologies are inherently inefficient due to the low levels of chrome fixed in the tanning bath, coupled with "bleeding out" of the chrome in subsequent processes **(UNEP IE/PAC, 1991)**.

Compounds of trivalent chromium are the most widely applied tanning agents and no significant changes are to be expected in the near future. During the last few years, some improvements in chrome tanning have been developed, tested and evaluated with respect to their operational difficulties, efficiency, economic viability, safety and effects on the leather quality. The use of such procedures permits tanneries to reduce the chromium discharge to the environment and improve the efficiency in the use of chemicals **(PTA/LIDO, 1995)**.

1. Direct Recycling of Chrome Tanning Float

Direct recycling of tanning floats remains the easiest method to apply for recovery and reuse of chromium salts from tanning operations. After collection and sufficiently fine screening, the floats are controlled and the chromium amounts used in the previous cycle are replaced by chromium salts. Depending on the tanning technology in use, the degree of exhaustion reached for each cycle may vary. In a conventional bovine tanning process, it is estimated that the direct recycling technology can save about 20 % of the chromium used in the conventional process

On the other hand, for the treatment of wooly sheep skins (especially double face), this direct recycling makes it possible to reuse almost 50 % of the chromium introduced in the process, since tanning floats do not reach exhaustion rates. This recycling method may be repeated several times on the same float. However, it is limited by the occurrence of quality problems with delicate hides, and by the need to control residual floats (acidity and chromium concentration)

Many, bovine and sheep skins tanneries have experimental with this technology and used it for several years. This technology is especially adopted by small firms and is widely used throughout Europe

Although the system does not completely eliminate the chromium being discharged through the effluent or sludge, it can be seen as a part of a general environmental plan of a tannery. Because it reduces the necessary amount of chromium being discharged to the environment, thus facilitating the treatment and disposal of a small amount of chromium containing sludge

2. Recycling After Precipitation

This is the old and most conventional method. It allows collection of the tanning float along with the rinses, that sometimes occur at the end of the tanning, and the effluent from various post-tanning stages (washing, dripping, sammying, etc). After collection, screening and storage, the floats are precipitated with different types of coagulants including sodium hydroxide, sodium carbonate, magnesium oxide, and even lime when recycling is not possible. A flocculation with polyelectrolyte may follow

The reuse of sludge after simple settling and acidification has been experimental and practiced. However, the normal process consists of settling the chromium sludge and treating it on a filter-press or vacuum filter

Large plants have operated under this scheme for many years in Germany, Italy, South America and France

Only large plants treating significant amounts of chromium can justifiably use the technology of recycling after precipitation and dewatering of the sludge. As a result, tanners collect their tanning residual bath for a common treatment. Small scale tanneries are using magnesium oxide precipitation and direct redissolution of the settled sludge for reuse as a tanning residual bath for a common treatment

Besides, the recycling after precipitation method can also be practiced as a treatment of chromium containing floats. Both systems, if conducted properly, can meet the limits demanded by most of the actual legislation for trivalent of chromium in effluent. However, most chemicals used in the process increase the salinity of the effluent

Chromium recycling is not recommended for effluent containing residues of surfactants, fat liquors and tanning agents other than chromium. So retanning floats cannot be treated by chromium recycling. In the case of treatment of more complex chromium containing floats, for example of retanning floats, chromium containing floats can be precipitated with calcium hydroxide and flocculants, followed by a separation and sludge drying by filter press or remaining overnight in a tank. The separated liquid phase can be discharged to the effluent and the remaining chromium sludge can be disposed of. It is, therefore, very important to avoid mixing of floats

### 3. Tanning Products that Improve the Exhaustion Rate

For the past few years, tanning and basification products have been available in the market which enable a tanning cycle inducing only small chromium wastes. These products are developed with the aim of bringing about the complete fixation of the chrome onto the protein fibers so that the exhausted chrome tanning float contains little or no chrome. It has the great advantage that no chrome losses are incurred by chrome liquor left in the tanned hide to be removed by subsequent machine squeezing or washing. Chrome take-up of over 90 % with exhaust of less than 1g per liter is possible. It is; therefore, possible to reduce the initial chrome oxide offer to about 1.8 % on the fleshed weight and still obtain the same amount of chrome fixed on the fiber

Tanning with such products can only be performed on split hides since the molecules are too large to penetrate adequately in the hide close to the grain side. When hides are split, the hides' reduced thickness makes this operation easier

Tanning with high exhaustion chromium salts requires extensive monitoring and is rather difficult to control. Care must be taken so that the chromium penetrates deeply in the hide before fixing, otherwise marks may appear on the grain side **(PTA/LIDO, 1995).**

Chrome fixation during tannage is favoured by short float, increased temperature, increased time of tanning, increased basification and decrease in neutral salts **(UNEP IE/PAC, 1991)**.

## A1.1.7.2 Vegetable Tanning

### A1.1.7.2.a Environmental impacts

The vegetable tanning agents produce a higher pollution load than chrome tanning agents although the latter have particular problems of their own. Spent tannin liquors cause very high COD value and persistently colored effluents. Furthermore, the degradation of tannin in conventional wastewater treatment is a slow and costly process

5 % Calgon and the limed pelts is delimed at pH 2.8 to 3.0 by an addition of sulfuric acid. An open pit pickle is usually necessary to ensure pH near 3 and equilibrium. The spent pickle liquor is kept and refortified by the addition of

approximately 2.25 % Calgon on limed weight and about 1-1.5 % sulfuric acid. These quantities are finalized by the tanner to best suit his individual preferences

Drained pickled pelt is transferred to a warm vegetable tan with a pH of between 3.2 and 3.5 and a density of approximately 1.1 or 100° barkometer. The temperature is kept at about 35°C. Tanning was originally developed for Mimosa, but since then it has been adapted to a number of different tanning materials. The vegetable tanning liquor maintains its strength by refortifying with the addition of more vegetable tanning material. The solutions stabilize on each repetitive bath. The quantity of Calgon in the tanning bath will be maintained at slightly less than 1 %. The pH will stabilize between 3.2 and 3.5 as desired

In some cases, it has been found convenient to use three steps. Between the Calgon pickle bath and the warm vegetable tanning bath, a vegetable tanning step is added, using a coloring vegetable bath of about 20° barkometer. This step produces slightly better leather, and is easier to control. However, it will result in some effluent, since the intermediate stage may not refortified and maintain consistence concentration in low strength liquors **(PTA/LIDO, 1995)**.

## A1.1.8 Wet Finishing: Retanning, Dyeing and Fatliquoring Process

### A1.1.8.a Environmental impacts

Usually retanning and wet finishing (dyeing, fatliquor) are conducted in a single float and result in an effluent containing residue of dyes, fatliquors and retanning agents. Chromium may be present in the float due to the presence of unfixed chromium in the wet-blue stocks. The use of very harmful chemicals for retanning fatliquoring and dyeing processes does have unavoidable impacts on the environment. Foe example chromium, lead and cadmium salts can still be found in some types of older dyes and pigments. Unused phenol based retanning agent, if discharged in the water containing fish, can cause the tanning of sensitive protein of fish. Some azo-dyes, containing carcinogenic amino-components like benzidine, are also in use in some countries. Fatliquoring oils used in the tannery are often composed of chlorinated alkane sulfonate and fatty acid methylester sulfonate that are now questionable because of the organic halogens quantities they can generate **(PTA/LIDO, 1995)**.

### A1.1.8.b Clean technology options

It can be concluded that the proper penetration of the materials used in tanning processes is very important factor for the proper utilization of the chemicals and also for avoiding their serious environmental impacts. The process has to be performed in a manner that assures the highest possible exhaust of the float. Metal complex dyes, which contain restricted heavy metals and benzidine based dyes, must be replaced. Handling of dyes in dry powder form demands protective equipment to avoid inhalation or skin contacts during the preparation of the formulation. The absorbable organic halogens, the chlorinated fatliquoring products will be replaced. Various substitutes are available commercially for this purpose. Some of the products have been developed which must be added to the fatliquoring oils. The oils are then converted into micro emulsions producing a significant reduction of COD in fatliquoring wastewater

The use of stainless steel drum with three compartments is suitable. The continuous mechanical action on the hides, the changing of the drums' rotation, the constant temperature and recycling of the bath from the bottom to the top, improve the efficiency of chemicals' penetration into the hides. This type of equipment has proven to be particularly interesting from environmental point of view, as they permit dye savings (heating the bath at the end of the process increases the exhaustion for 15 or 20 %). In addition, they enable dyeing in a very short float and require lower quantities of water for rising. The rate of water in the float is only 100 % of the wet blue weight, whereas, it is 400 % in the classic drums. Thus, the discharge load is reduced by 50 % and the product exhaustion rate reaches 90 %. Finally, controls are eased during rather complicated process of dyeing

The cost of three compartment drum is very high, but the duration of the whole process can be shorten, compared to a classical drum **(PTA/LIDO, 1995)**.

## A1.1.9 Drying of Leather

### A1.1.9.a Environmental impacts

No environmental impacts are reported in the literature for drying operation

### A1.1.9.a Clean technology options

The air drying system is the cleanest method

## A1.1.10 Finishing

### A1.1.10.a Environmental impacts

The environmental impact of finishing operations is mainly related to the finishing chemicals (e.g. dyes and pigments dispersed in a binder) which can reach effluent water or are emitted to the air, like solvent vapors or formaldehyde, which also causes occupational health problems **(PTA/LIDO, 1995)**.

### A1.1.10.b Clean technology options

Halogen containing hydrocarbons have to be replaced by water based finishers. Metal complex dyes which contain restricted heavy metals have to be avoided, as well as aziridine based cross linking products. Formaldehyde should be controlled well or replaced by other kinds of preservatives with lower environmental and occupational implication, like the use of ammonia in finishing solutions

Roll coating results in reduction of VOCs in the work place and financial savings

Filters for dust control in the buffering units, aerators in the finishing working rooms and activated carbon filter in the exhaustion of the finishing equipment are recommendable procedures for keeping finishing air emission under control. The buffing process generates dust in the dry form. This dust can be used as a flocculating agent in sedimentation tanks or as a filer in the manufacture of certain plastic articles. If the dust is from chrome-tanned leather, it may be treated with other chrome containing solid waste

Conventional spray equipment is wasteful, between 30% and 50% of finish is usually lost, whereas, with the use of a roll coating machine, looses may be reduced to as low as 5%. Large tanneries and some of the medium size tanneries may be able to change the conventional spray equipment

Exhaustion from plants and drying tunnels, which are in use, can be improved by efficient scrubbing to clear the air emission. Plants without scrubbing system should install this system **(PTA/LIDO, 1995)**.

# Appendix Two

## General Safety Measures

# A2.1 GENERAL SAFETY MEASURES IN TANNERIES

Safety conditions are generally associated with the protection from machine operations handling of hides and skins, chemicals used in the tannery, and hazards of chemicals generated during different tannery processes. In Palestine, following measures are necessary to be adopted in order to improve the overall-working environment

## A2.1.1 Equipment and Machinery

If machinery and equipment of the tannery are being operated by two workers, both have to release the start button for operation, but switch off must be possible by releasing one button only. Moving parts of the cylinder machine (fleshing, unhairing, stretching, smoothing and sammying machine) must be protected in such a manner that parts of the body do not come in contact with these machine parts. Splitting machine must be equipped with sufficient shielding for knives. Sharpening, buffing and brushing machine must be equipped with complete railing and covering. Drums must be equipped with shields or covers for the gear drive and in general, a railing to ensure a certain distance should be provided. A mechanical device to fix the drums safely during filling or cleaning procedures must be present

Movable machine parts (like drums and mixers, gear wheels, conveyor belts or cylinder machine) must be shielded and provision should be made for the machine to operate only is the shield device is closed. Same safety precaution is associated with the machine performing movements with force and the machine working with heat. In addition, these machined must be equipped with an emergency switch. If the procedure is performed with both hands, releasing of the switch must be possible with another part of the body. Hot surface on the machine must be protected against contact

Floors have to be kept clean and dry, thus reducing the hazards of stumbling and slipping. A high degree of noise level during short or long periods may lead to defective hearing and functional defects of the brain. Measures for noise abatement have to be taken as much as possible, like shielding of engines and machines **(PTA/LIDO, 1995)**.

## A2.1.2 Handling of Chemical Used in the Tannery

The following suggestions are made which will be helpful in improving of the In-house practices and in reducing the health hazards for the workers

A number of different chemicals are used in the tannery. These chemicals are different in nature and characteristics, therefore, their handling, collection and disposal must be performed with respect to their specific characteristics and hazards, empty vessels or containers must not be dumped since they still contain small amounts of chemicals which need to be disposed off properly

Workers must be provided with protective devices depending on the working places (gloves, protective clothing, protective goggles, etc).

Materials for cleaning and skin protection (protective cream, special soap) must be available. Parts of the body, especially eyes, contaminated with chemicals, have to be cleaned thoroughly with clean water

Following precautions against fire and explosion risk have to be taken:

1. Inflammable chemicals should not be stored at the working place, but in the store room
2. Places involving fire risks must be indicated by symbolic signs
3. Open fire or any other sources of ignition (smoking) are prohibited at working places where inflammable substances are used
4. Inflammable wastes and material must be kept away from working places

General chemicals used in tanneries and their handling are described below

**Acids and Bases**

This group contains calcium hydroxide and alkali hydroxide (used for soaking and unhairing), sulfuric acid, hydrochloric acid, formic acid (pickle), and other organic acids

Acids and bases irritate skin and eyes and are more or less caustic. Their vapors irritate mucous membranes and respiratory tract

Precautions against any direct contact have to be taken (gloves, resistant clothing, efficient ventilation, etc.)

Due to inflammable nature of formic acid, any fire in the working area must be prohibited

Pouring of water into an acid for dilution must be avoided. Dilution is always carried out by pouring acid into water

**Sodium Sulfide, Sodium Hydrogen Sulfide**

Both compounds are caustic. They should never come in contact with acids, because the reaction generates highly toxic hydrogen sulfide

Precautions against any direct contacts have to be taken for which the gloves, resistant clothing, efficient ventilation are required

**Tanning Agents (Chrome Tanning)**

Basic chromium sulfate, chromium (III) oxide salt, is used for tanning purpose. Care must be taken to avoid risks of explosions of dust and toxic hazards if the dust is inhaled. Therefore, it will be better to use suspensions of chromium salts

Careful handling is essential, direct skin contact should be avoided. Chromium (VI) compounds are highly toxic and cause cancer. The use of these compounds must be stopped in the tanneries

**Tanning Agents (Vegetable Tanning)**

This group contains a variety of complex organic molecules. As in general, direct contact with the skin has to be avoided. Any handling must be performed carefully

**Chemicals Used for Finishing**

This group of chemicals includes dyes, polymers, preservatives and other groups of compounds. The agents used for the various steps of finishing are often combinations of several organic compounds or solution in water or in organic solvents

In general, precautions against skin contact must be taken

Efficient exhaust devices must be provided to minimize the concentrations of organic solvents or dust from powders in the working environment

It is recommended to use the agents in accordance with the instructions given by the producer

Smoking must be prohibited in this area

**Dyes**

Dyes must be handled carefully, with due consideration being given to characteristics and hazards. After skin's contact, thorough cleaning with water and soap must be performed. Especially eyes have to cleaned intensively and doctor must be consulted

It is very important to store dyes in perfectly closed containers. If dyes are spilled, they have to be collected dryly and filled into closed containers

It is highly recommended to cease the use of benzidine dyes because they are highly carcinogenic

**Formaldehyde**

In many cases formaldehyde is emitted during finishing processes especially during drying of finished leather. In higher concentration, it is a strong acute toxin, causes skin allergies, leads to coughs, spasms of the respiratory tract, chemicals induced pneumonia and the sensibilisation of the respiratory tracts. Furthermore, it is under suspicion to cause cancer

**Pentachlorophenol**

The use of PCP for preservation is forbidden in Europe and many other countries and must be ceased in the local tanneries **(PTA/LIDO, 1995)**.

## A2.1.3 Chemicals Generated in Tanning Processes

As a result of the present practices and absence of any remedial measure in the Palestine tanneries, many hazardous gases are produced. To reduce their hazards and complete elimination is only possible after the adoption of the clean technologies in the tanneries. Sections below explain the remedial measures for each gas

**Hydrogen Sulfide**

The generation of hydrogen sulfide is basically due to the use of sodium sulfide and sodium hydrogen sulfide during unhairing. It starts at a pH below 10. If washing after unhairing is not performed properly, the risk of hydrogen sulfide generation starts even in the deliming process, but at least during pickling due to the addition of the acids

It is possible that high amount of this toxic gas is present within drums or mixers and it is distributed in the plant through the hollow axis or the opening of the drum. Besides, the gas might be generated in pits, effluent channel and effluent collection basins

Hydrogen sulfide and air are highly explosive in mixture from 4.3 to 45.5 vol%, therefore, open fire or other source of ignition must be avoided

In addition, the gas narcotizes the sense of smell even in low amount. This means, that the worker is after a short time, no longer aware of being exposed to this toxic compound and might be poisoned to a high degree

The following measures are recommended to avoid the possibility of hydrogen sulfide formation

- Application of low sodium sulfide unhairing processes
- Thorough washing of pits with water (2-3 times water: 200 %, 30 °C)
- Use of manganese sulfate/oxygen, sodium sulfite or sodium hypochlorite during deliming in order to oxidize hydrogen sulfide
- Efficient ventilation of the plant

- Thorough washing after deliming/bating

**Ammonia**

The generation of ammonia is possible during deliming. This gas is very caustic, toxic if breathed in and inflammable

Precautions need to be taken to avoid the generation, like change in deliming agents

**Gases from Bleaching Process**

Bleaching process after vegetable tanning process is a major cause of producing very corrosive gases like $SO_2$ and $SO_3$. The workers may be affected badly with these gases. Use of bleached vegetable tanning material can help to avoid the formation of these gases. Otherwise workers should be provided with special masks, capable of providing protection against these gases **(PTA/LIDO, 1995)**.

## A2.2 CONCLUSIONS AND RECOMMENDATIONS

The proposed recommendations will be in two major areas. These are change in processing practices, and use of alternative technologies. Following are the specific conclusions and recommendations for improvement in practices and adoption of alternative technologies:

### A2.2.1 Improvement in Practices

**Curing**

In the short run, it is not possible to substitute salt curing by any other known practice, therefore, practices of salt recovery and minimization explained above should be adopted

Wherever efficient transportation of skins and hides is possible here in Palestine, the practice of using fresh skins or chilled skins should be promoted

### Soaking

Water conservation should be promoted. The options of performing soaking and unhairing in a single batch, and green fleshing just after the deep soak, should also be promoted

### Unhairing and Liming

Hair saving system, recycling of liming liquor, sulfide oxidation, and lime splitting and trimming should be promoted

### Deliming and Bating

Use of sodium bisulfite or hydrogen peroxide before addition of the deliming chemicals should be promoted. This would help in the oxidation of sulfide

The option of using weak acid for deliming and bating has also demonstrated good results. This option need to be promoted

Water conservation can be introduced at this stage by shifting from washing through continuous flow of water to batch washing. It is estimated that adoption of this practice will reduce 50 % of present level of water consumption in tanneries

### Degreasing

The use of alcohol ethoxylate based surfactant should be used by all medium and large tanneries.

### Wet Finishing

The use of halogenated fatliquors, benzidine based dyes, etc. should be banned. Instead, high fixing polymeric auxiliaries which are easily available in the local market should be promoted. These auxiliaries are not also high fixing, however, they perform an additional function of retanning and fat liquoring agents, hence reduce the pollution load. Precondition to this practice is to control the pH of the solution above 4; otherwise it will support the release of chromium in the solution

### Finishing

The halogen containing hydrocarbons should be replaced by water based finishers. The use of metal complex dyes which contain restricted heavy metals should be abandoned, instead other environmentally friendly chemicals should be used

The labor should be properly trained in handling chemicals with the help of occupational and safety equipment **(PTA/LIDO, 1995)**.

## A2.2.2 Adoption of Alternative Technologies

### Curing

In the long run, the environmental legislation will be much more stringent that the existing legislation. In future, tanners have to adopt better friendly cleaner technologies. Arrangement should be made now for the introduction of new curing technologies to the tanners.

### Unhairing and Liming

The new efficient alternative technologies of lime sulfide processes should be demonstrated to the tanners in Palestine

### Deliming and Bating

The technology of deliming through carbon dioxide showed good results for large tanneries. This technology should be demonstrated to the large tanneries in Palestine

### Degreasing

All medium and large tanneries should install adequate equipments for storage, recovery and regeneration of solvents. With the recycling of extract brines, recapturing of grease, and control on the vaporization of solvents, many occupational health problems can be solved

### Pickling

Recycling of pickling floats is a common practice in many tanneries all over the world. In Palestine, pickling and tanning are simultaneously carried out. Therefore, recycling of the pickling float can be done along with chrome recovery

### Chrome Tanning

It is recommended that all the tanneries should install chrome recovery and reuse plants by which chromium salts are precipitated and then reused

### Finishing

Conventional spray equipments should be replaced with roll coating machines. Conventional sprays waste about 30 % to 50 % of the finishing material. The roll coating machine reduces the wastage to only 5 %

Efficient scrubbers should be installed at finishing spray plant and proper ventilation at the place of spray plants **(PTA/LIDO, 1995)**.

# Appendix Three

## Analytical Methods

# A3.1 pH

## Principle

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment, e.g., acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control, is pH-dependent. pH is used in alkalinity and carbon dioxide measurements and many other acid-base equilibria. At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Alkalinity and acidity are the acid- and base-neutralizing capacities of a water and usually are expressed as milligrams $CaCO_3$ per liter. Buffer capacity is the amount of strong acid or base, usually expressed in moles per liter, needed to change the pH value of a 1 L sample by 1 unit. pH as defined by Sorenson is -log [H+]; it is the "intensity" factor of acidity. Pure water is very slightly ionized and at equilibrium the ion product is

$[H+][OH-] = Kw$
$= 1.01 X 10 - 14$ at 25°C

$[H^+] = [OH^-]$
$= 1.005 \times 10^{-7}$

where
$[H^+]$ = activity of hydrogen ions, moles/L,
$[OH^-]$ = activity of hydroxyl ions, moles/L, and
Kw = ion product of water.

At 25°C, pH 7.0 is neutral, the activities of the hydrogen and hydroxyl ions are equal, and each corresponds to an approximate activity of $10^{-7}$ moles/L. The neutral point is temperature-dependent and is pH 7.5 at 0°C and pH 6.5 at 60°C.

The pH value of a highly dilute solution is approximately the same as the negative common logarithm of the hydrogen ion concentration. Natural waters usually have pH values in the range of 4 to 9, and most are slightly basic because of the presence of bicarbonates and carbonates of the alkali and alkaline earth metals.

## Electrometric Method

### General Discussion

Principle: The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Because single ion activities such as $aH^+$ cannot be measured, pH is defined operationally on a potentiometric scale. The pH measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using National Institute of Standards and Technology (NIST, formerly National Bureau of Standards) buffers having assigned values.

## A3.2 Conductivity

### Introduction

Conductivity, k, is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence; and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

### Definitions and Units of Expression

Conductance, G, is defined as the reciprocal of resistance, R:

$$G = \frac{1}{R}$$

where the unit of R is ohm and G is $ohm^{-1}$ (sometimes written mho). Conductance of a solution is measured between two spatially fixed and chemically inert electrodes. To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current signal. The conductance of a solution, G, is directly proportional to the electrode surface area, $A$, $cm^2$ , and inversely proportional to the distance between the electrodes, L, cm. The constant of proportionality, k, such that:

$$G = k \frac{A}{L}$$

is called "conductivity" (preferred to "specific conductance"). It is a characteristic property of the solution between the. electrodes. The units of k are l/ohm-cm or mho per centimeter. Conductivity is customarily reported in micromhos per centimeter (μmho/cm).

In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as millisiemens per meter (mS/m); 1 mS/m = 10 umhos/cm and 1 uS/ cm = 1 umho/cm. To report results in SI units of mS/m divide umhos/cm by 10.

To compare conductivities, values of k are reported relative to electrodes with A = 1 $cm^2$ and L = 1 cm. Absolute conductances, Gs, of standard potassium chloride solutions between electrodes of precise geometry have, been measured; The equivalent conductivity, A, of a solution is the conductivity per unit of concentration. As the concentration is decreased toward zero, A approaches a constant, designated as A°. With k in units of micromhos per centimeter it is necessary to convert concentration to units of equivalents per cubic centimeter; therefore:ΛΛΛΛ

A = 0.001k/concentration

where the units of A, k, and concentration are mho-$cm^2$/equivalent, umho/cm, and equivalent/L, respectively.

## Measurement

Instrumental measurements: In the laboratory, conductance, Gs, (or resistance) of a standard KCl solution is measured and from the corresponding conductivity, ks, a cell constant, C, cm - 1, is calculated:

$$C = \frac{k_s}{G_s}$$

Most conductivity meters do not display the actual solution conductance, G, or resistance, R; rather, they generally have a dial that permits the user to adjust the internal cell constant to match the conductivity, $k_s$, of a standard. Once the cell constant has been determined, or set, the conductivity of an unknown solution,

$k_u = CG_u$,

will be displayed by the meter.

Distilled water produced in a laboratory generally has a conductivity in the range 0.5 to 3 umhos/cm. The conductivity increases shortly after exposure to both air and the water container.

The conductivity of potable waters in the United States ranges generally from 50 to 1500 umhos/cm. The conductivity of domestic wastewaters may be near that of the local water supply, although some industrial wastes have conductivities above 10 000 umhos/cm. Conductivity instruments are used in pipelines, channels, flowing streams, and lakes and can be incorporated in multiple-parameter monitoring stations using recorders.

## A3.3 Salinity

### General Discussion

Salinity is an important unitless property of industrial and natural waters. It was originally conceived as a measure of the mass of dissolved salts in a given mass of solution. The experimental determination of the salt content by drying and weighing presents some difficulties due to the loss of some components. The only reliable way to determine the true or absolute salinity of a natural water is to make a complete chemical analysis. However, this method is time-consuming and cannot yield the precision necessary for accurate work. Thus, to determine salinity, one normally uses indirect methods involving the measurement of a physical property such as conductivity, density, sound speed, or refractive index. From an empirical relationship of salinity and the physical property determined for a standard solution it is possible to calculate salinity. The resultant salinity is no more accurate than the empirical relationship. The precision of the measurement of a physical property will determine the precision in salinity. Following are the precisions of various physical measurements and the resultant salinity presently attainable with commercial instruments:

Although conductivity has the greatest precision, it responds only to ionic solutes. Density, although less precise, responds to all dissolved solutes.

## Selection of Method

In the past, the salinity of seawater was determined by hydrometric and argentometric methods. In recent years the conductivity and density methods have been used because of their high sensitivity and precision. These two methods are recommended for precise field and laboratory work.

# A3.4 Solids

## Introduction

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be aesthetically unsatisfactory for such purposes as bathing. Solids analyses are Important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

## Definitions

"Total solids" is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes "total suspended solids", the portion of total solids retained by a filter, and "total dissolved solids," the portion that passes through the filter.

The type of filter holder, the bore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. "Dissolved solids" is the portion of solids that passes through a filter of 2.0 um (or smaller) nominal bore size under specified conditions. "Suspended solids" is the portion retained on the filter.

"Fixed solids" is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called "volatile solids." Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts. Better characterization of organic matter can be made by such tests as total organic carbon, BOD and COD.

"Settleable solids" is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique.

## Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 hours. In no case hold sample more than 7 days. Bring samples to room temperature before analysis.

## Total Solids Dried at 103-105°C

## General Discussion

Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of actual dissolved and suspended solids in wastewater samples.

Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

## Apparatus

1. Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:
   - Porcelain, 90-mm diam.
   - Platinum-Generally satisfactory for all purposes.
   - High-silica glass.

2. Muffle furnace for operation at 500 ± 50°C.
3. Steam bath.
4. Desiccator, provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator.
5. Drying oven, for operation at 103 to 105°C.
6. Analytical balance, capable of weighing to 0.1 mg.
7. Magnetic stirrer with TFE stirring bar.
8. Wide-bore pipets.

## Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at 500 ± 50°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105'C for 1 h. Store and cool dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 10 and 200 mg. When very low total suspended solids are encountered (less than 10 mg/L), less residue may be collected; compensate by using a high-sensitivity balance (0.002 mg). Pipet a measured volume of well-mixed sample to a preweighed dish and evaporate to dryness on a steam bath or in a drying oven. Stir sample with a magnetic stirrer during transfer. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drying oven, lower temperature to approximately 2'C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105'C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation. Duplicate determinations should agree within 5% of their average.

## Calculation

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

$A$ = weight of dried residue + dish, mg, and

$B$ = weight of dish, mg.

## Total Dissolved Solids Dried at 180°C

### General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures.

The results may not agree with the theoretical value for solids calculated ' from chemical analysis of sample. Approximate methods for correlating chemical analysis with dissolved solids are available. The filtrate from the total suspended solids determination may be used for determination of total dissolved solids.

b. Interferences Highly mineralized waters with a considerable calcium, magnesium, chloride, and/ or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

### Apparatus

a. Glass-fiber filter disks without organic binder.

b. Filtration, apparatus: One of the following, suitable for the filter disk selected:

1) Membrane filter funnel.

2) Gooch crucible, 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) Filtration apparatus with reservoir and coarse (40- to 60-µum) fritted disk as filter support.

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

## Procedure

a. Preparation of glass-fiber filter disk: Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 500 ± 50°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 10 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume. When very low total suspended solids are encountered (less than 10 mg/L), less dried residue may be collected; compensate by using a high-sensitivity balance (0.002 mg)

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume. onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath. If filtrate volume exceeds dish capacity add successive portions to the same dish after evaporation. Dry for at least 1 h in an oven at 180 ± 20°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Duplicate determinations should agree within 5% of their average.

## Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and

$B$ = weight of dish, mg.

## Total Suspended Solids Dried at 103-105°C

## General Discussion

a. Principle: A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, the difference between the total solids and the total dissolved solids may provide an estimate of the total suspended solids.

b. Interferences: Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

## Procedure

a. Preparation of glass-fiber filter disk: Insert disk with wrinkled side up in filtration apparatus. Apply vacuum and wash disk with three successive 20-mL portions of reagent-grade water.

Continue suction to remove all traces of water, and discard washings. Remove filter from filtration apparatus and transfer to an inert planchet. Take care to prevent the dried filter from adhering to the planchet. Alternatively weigh dried filter and planchet both before and after filtration. Filter material that sticks to the dish remains with the filter and avoids error. If a Gooch crucible is used, remove crucible and filter combination. Dry in an oven at 103 to 105'C for 1 h. If volatile solids are to be measured, ignite at 500 ± 50°C for 15 min in a muffle furnace. Cool in desiccator to balance temperature and weigh. Repeat cycle of drying or igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Store in desiccator until needed.

b. Selection of filter and sample sizes: For nonhomogeneous samples such as raw wastewater, use a large filter to permit filtering a representative sample.

c. Sample analysis: Assemble filtering apparatus and filter and begin suction. Wet filter with a small volume of reagent-grade water to seat it. Stir sample with a magnetic stirrer, and while stirring, pipet a measured volume onto the seated glass-fiber filter. Wash with three successive 10-mL volumes of reagentgrade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Samples with high dissolved solids may require additional washings. Carefully remove filter from filtration apparatus and transfer to an aluminum or stainless steel planchet as a support. Alternatively, remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used. Dry for at least 1 h at 103 to 105°C in an oven, cool in a desiccator to balance temperature, and weigh. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg, whichever is less. Duplicate determinations should agree within 5% of their average.

### Calculation

$$\text{mg total suspended solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

$A$ = weight of filter + dried residue, mg, and

$B$ = weight of filter, mg.

## A3.5 DO and BOD

"Dissolved Oxygen and Biochemical Oxygen Demand"

### A3.5.1 DISSOLVED OXYGEN

### Significance

Dissolved oxygen (DO) levels in natural and wastewaters depend on the physical, chemical, and biochemical activities in the water body. The analysis for DO is a key test in water pollution and waste treatment process control.

### Selection of Method

Two methods for DO analysis are described: the Winkler or iodometric method and its modifications and the electrometric method using membrane electrodes. The iodometric method is a titrimetric procedure based on the oxidizing property of DO while the membrane electrode procedure is based on the rate of diffusion of molecular oxygen across a membrane.

The choice of procedure depends on the interferences present, the accuracy desired, and, in some cases, convenience or expedience.

## Iodometric Methods

### Principle

The iodometric test is the most precise and reliable titrimetric procedure for DO analysis. It is based on the addition of divalent manganese solution, followed by strong alkali, to the sample in a glass-stoppered bottle. DO rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides of higher valency states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of thiosulfate.

The titration end point can be detected visually, with a starch indicator, or electrometrically, with potentiometric or dead-stop techniques.

The liberated iodine also can be determined directly by simple absorption spectrophotometers. This method can be used on a routine basis to provide very accurate estimates for DO in the microgram-per-liter range provided that interfering particulate matter, color, and chemical interferences are absent.

### Selection of Method

Before selecting a method consider the effect of interferences, particularly oxidizing or reducing materials that may be present in the sample. Certain oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Most organic matter is oxidized partially when the oxidized manganese precipitate is acidified, thus causing negative errors.

Several modifications of the iodometric method are given to minimize the effect of interfering materials. Among the more commonly used procedures are the azide modification, the permanganate modification, the alum flocculation modification, and the copper sulfate-sulfamic acid flocculation modification. The azide modification effectively removes interference caused by nitrite, which is the most common interference in biologically treated effluents and incubated BOD samples.

## Collection of Samples

Collect samples very carefully. Methods of sampling are highly dependent on source to be sampled and, to a certain extent, on method of analysis. Do not let sample remain in contact with air or be agitated, because either condition causes a change in its gaseous content. Samples from any depth in streams, lakes, or reservoirs, and samples of boiler water, need special precautions to eliminate changes in pressure and temperature. Procedures and equipment have been developed for sampling waters under pressure and unconfined waters (e.g., streams, rivers, and reservoirs).

Collect surface water samples in narrow-mouth glass-stoppered BOD bottles of 300-mL capacity with tapered and pointed ground-glass stoppers and flared mouths. Avoid entraining or dissolving atmospheric oxygen. In sampling from a line under pressure, attach a glass or rubber tube to the tap and extend to bottom of bottle. Let bottle overflow two or three times its volume and replace stopper so that no air bubbles are entrained.

## Preservation of Samples

Determine DO immediately on all samples containing an appreciable oxygen or iodine demand. Samples with no iodine demand may be stored for a few hours without change after adding manganous sulfate ($MnSO_4$) solution, alkali-iodide solution, and $H_2S0_4$ followed by shaking in the usual way. Protect stored samples from strong sunlight and titrate as soon as possible.

For samples with an iodine demand, preserve for 4 to 8 h by adding 0.7 mL conc $H_2S0_4$ and 1 mL sodium azide solution (2 g $NaN_3$/100 mL distilled water) to the BOD bottle. This will arrest biological activity and maintain DO if the bottle is stored at the temperature of collection or water-sealed and kept at 10 to 20°C. As soon as possible, complete the procedure, using 2 mL $MnSO_4$ solution, 3 mL alkali-iodide solution, and 2 mL conc $H_2S0_4$.

## Azide Modification

### General Discussion

Use the azide modification for most wastewater, effluent, and stream samples, especially if samples contain more than 50 ug $NO_2$ –N/L and not more than 1 mg ferrous iron/L. Other reducing or oxidizing materials should be absent. If 1 mL KF solution is added before the sample is acidified and there is no delay in titration, the method is applicable in the presence of 100 to 200 mg ferric iron/L.

## Reagents

a. Manganous sulfate solution: Dissolve 480 g $MnSO_4.4H_2O$, 400 g $MnSO_4.2H_2O$. or 364 g $MnSO_4.H_20$ in distilled water, filter. and dilute to 1 L. The $MnSO_4$ solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.

b. Alkali-iodide-azide reagent

1) For saturated or less-than-saturated samples-Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in distilled water and dilute to 1 L. Add 10 g $NaN_3$, dissolved in 40 mL distilled water. Potassium and sodium salts may be used interchangeably. This reagent should not give a color with starch solution when diluted and acidified.

2) For supersaturated samples-Dissolve 10 g $NaN_3$ in 500 mL distilled water. Add 480g sodium hydroxide (NaOH) and 750g sodium iodide (NaI) and stir until dissolved. There will be a white turbidity due to sodium carbonate ($Na_2CO_3$), but this will do no harm. CAUTION-Do not acidify this solution because toxic hydrazoic acid fumes may be produced.

c. Sulfuric acid, $H_2SO_4$, conc: One milliliter is equivalent to about 3 mL alkali-iodide-azide reagent.

d. Starch: Use either an aqueous solution or soluble starch powder mixtures.

To prepare an aqueous solution, dissolve 2 g laboratory-grade soluble starch and 0.2 salicylic acid as a preservative, in 100 mL hot distilled water.

e. Standard sodium thiosulfate titrant: Dissolve 6.205 g $Na_2S_2O_3.5H_20$ in distilled water. Add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution.

f. Standard potassium bi-iodate solution, 0.0021M: Dissolve 812.4 mg $KH(I0_3)_2$ in distilled water and dilute to 1000 mL.

Standardization: Dissolve approximately 2 g KI, free from iodate, in an erlenmeyer flask with 100 to 150 mL distilled water. Add 1 mL 6N $H_2SO_4$ or a few drops of conc $H_2SO_4$ and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate liberated iodine with thiosulfate titrant. Adding starch toward end of titration, when a pale straw color is reached. When the solutions are of equal strength, 20.00 mL 0.025M $Na_2S_2O_3$, should be required. If rot, adjust the $Na_2S_2O_3$ solution to 0.025M.

g. Potassium Sulfide solution.. Dissolve 40 g $KF.2H_20$ in distilled water and dilute to 100 mL.

## Procedure

a. To the sample collected in a 250- to 300-mL bottle, add 1 mL $MnSO_4$ solution, followed by 1 mL alkali-iodide-azide reagent. If pipets are dipped into sample, rinse them before returning them to reagent bottles. Alternatively, hold pipet tips just above liquid surface when adding reagents. Stopper carefully to exclude air bubbles and mix by inverting bottle a few times. When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernate above the manganese hydroxide floc, add 1.0 mL conc $H_2S0_4$. Restopper and mix by inverting several times until dissolution is complete. Titrate a volume corresponding to 200 mL original sample after correction for sample loss by displacement with reagents. Thus, for a total of 2 mL (1 mL each) of $MnSO_4$ and alkali-iodide-azide reagents in a 300-mL bottle, titrate 200 X 300/(300 - 2) = 201 mL.

b. Titrate with 0.025M $Na_2S_2O_3$ solution to a pale straw color. Add a few drops of starch solution and continue titration to first disappearance of blue color. If end point is overrun, back-titrate with 0.0021M bi-iodate solution added dropwise, or by adding a measured volume of treated sample. Correct for amount of biiodate solution or sample. Disregard subsequent recolorations due to the catalytic effect of nitrite or to traces of ferric salts that have not been complexed with fluoride.

## Calculation

For titration of 200 mL sample, 1 mL 0.025M $Na_2S_2O_3$ = 1 mg DO/L.

## A3.5.2 BIOCHEMICAL OXYGEN DEMAND

### General Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems. The test measures the oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. The seeding and dilution procedures provide an estimate of the BOD at pH 6.5 to 7.5.

Although only the 5-d BOD ($BOD_5$) is described here, many variations of oxygen demand measurements exist. These include using shorter and longer incubation periods, tests to determine rates of oxygen uptake, and continuous oxygen-uptake measurements by respirometric techniques. Alternative seeding, dilution, and incubation conditions can be chosen to mimic receiving-water conditions, thereby providing an estimate of the environmental effects of wastewaters and effluents.

## Carbonaceous Versus Nitrogenous BOD

Oxidation of reduced forms of nitrogen, mediated by microorganisms, exerts nitrogenous demand. Nitrogenous demand historically has been considered an interference in the determination of BOD, as clearly evidenced by the inclusion of ammonia in the dilution water. The interference from nitrogenous demand can now be prevented by an inhibitory chemical. 1 If an inhibiting chemical is not used, the oxygen demand measured is the sum of carbonaceous and nitrogenous demands.

Measurements that include nitrogenous demand generally are not useful for assessing the oxygen demand associated with organic material. Nitrogenous demand can be estimated directly from ammonia nitrogen; and carbonaceous demand can be estimated by subtracting the theoretical equivalent of the reduced nitrogen oxidation from uninhibited test results. However, this method is cumbersome and is subject to considerable error. Chemical inhibition of nitrogenous demand provides a more direct and more reliable measure of carbonaceous demand.

The extent of oxidation of nitrogenous compounds during the 5-d incubation period depends on the presence of microorganisms capable of carrying out this oxidation. Such organisms usually are not present in raw sewage or primary effluent in sufficient numbers to oxidize significant quantities of reduced nitrogen forms in the 5-d BOD test. Many biological treatment plant effluents contain significant numbers of nitrifying organisms. Because oxidation of nitrogenous compounds can occur in such samples, inhibition of nitrification is recommended for samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters. . Report results as CBOD, when inhibiting the nitrogenous oxygen demand. When nitrification is not inhibited, report results as $BOD_5$.

## Dilution Requirements

The BOD concentration in most wastewaters exceeds the concentration of dissolved oxygen (DO) available in an air-saturated sample. Therefore, it is necessary to dilute the sample before incubation to bring the oxygen demand and supply into appropriate balance. Because bacterial growth requires nutrients such as nitrogen, phosphorus, and trace metals, these are added to the dilution water, which is buffered to ensure that the pH of the incubated sample remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, 5 d has been accepted as the standard incubation period.

If the dilution water is of poor quality, effectively, dilution water will appear as sample BOD. This effect will be amplified by the dilution factor. A positive bias will result. The method included below contains both a dilution-water check and a dilution-water blank. Seeded dilution waters are checked further for acceptable quality by measuring their consumption of oxygen from a known organic mixture, usually glucose and glutamic acid.

The source of dilution water is not restricted and may be distilled, tap, or receiving-stream water free of biodegradable organics and bioinhibitory substances such as chlorine or heavy metals. Distilled water may contain ammonia or volatile organics; deionized waters often are contaminated with soluble organics leached from the resin bed. Use of copper-lined stills or copper fittings attached to distilled water lines may produce water containing excessive amounts of copper.

## 5-Day BOD Test

### General Discussion

a. Principle: The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 d. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because then initial DO is determined immediately after the dilution is made, all oxygen uptake, including that occurring during the first 15 min, is included in the BOD measurement.

b. Sampling and storage: Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analysing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20°C before analysis.

1) Grab samples-If analysis is begun within 2 h of collection, cold storage is unnecessary. If analysis is not started within 2 h of sample collection, keep sample at or below 4°C from the time of collection. Begin analysis within 6 h of collection; when this is not possible because the sampling site is distant from the laboratory, store at or below 4°C and report length and temperature of storage with the results. In no case start analysis more than 24 h after grab sample collection. When samples are to be used for regulatory purposes make every effort to deliver samples for analysis within 6 h of collection.

2) Composite samples- Keep samples at or below 4°C during compositing. Limit compositing period to 24 h. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the results.

## Apparatus

a. Incubation bottles, 250- to 300-mL capacity. Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a water-seal. Obtain satisfactory water seals by inverting bottles in a water bath or by adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over flared mouth of bottle to reduce evaporation of the water seal during incubation.

b. Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

### Reagents

a. Phosphate buffer solution: Dissolve 8.5 g $KH_2PO_4$, 21.75 g $K_2HPO_4$, 33.4 g $Na_2HPO_4.7H_2O$, and 1.7 g $NH_4Cl$ in about 500 ml distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Discard reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

b. Magnesium sulfate solution: Dissolve 22.5 $MgSO_4.7H_20$ in distilled water and dilute to 1 L.

c. Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

d. Ferric chloride solution: Dissolve 0.25 g $FeCl_3$,.$6H_20$ in distilled water and dilute to 1 L.

e. Acid and alkali solutions, IN, for neutralization of caustic and acidic waste samples.

1) Acid-Slowly and while stirring, add 28 mL conc sulfuric acid to distilled water. Dilute to 1 L.

2) Alkali-Dissolve 40 g sodium hydroxide in distilled water. Dilute to 1 L.

f. Sodium sulfite solution: Dissolve 1.575 g Na2SO3, in 1000 mL distilled water. This solution is not stable: prepare daily.

g. Nitrification inhibitor, 2-chloro-6-(trichloro methyl) pyridine.

h. Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent grade glutamic acid at 103°C for 1 h. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

i. Ammonium chloride solution: Dissolve 1.15 g $NH_4Cl$ in about 500 mL distilled water, adjust pH to 7.2 with NaOH solution, and dilute to 1 L. Solution contains 0.3 mg N/mL.

## Procedure

a. Preparation of dilution water: Place desired volume of water in a suitable bottle and add 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions/L of water. Before use bring dilution water temperature to 20°C. Saturate with DO by shaking in a partially filled bottle or by aerating with organic-free filtered air. Alternatively, store in cotton-plugged bottles long enough for water to become saturated with DO. Protect water quality by using clean glassware, tubing, and bottles.

Dilution technique: Dilutions that result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after 5 d incubation produce the most reliable results. Make several dilutions of prepared sample to obtain DO uptake in this range. Experience with a particular sample will permit use of a smaller number of dilutions. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilutions. In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for strong industrial wastes. 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

Prepare dilutions either in graduated cylinders and then transfer to BOD bottles or prepare directly in BOD bottles. Either dilution method can be combined with any DO measurement technique. The number of bottles to be prepared for each dilution depends on the DO technique and the number of replicates desired.

When using graduated cylinders to prepare dilutions, and when seeding is necessary, add seed either directly to dilution- water or to individual cylinders before dilution. Seeding of individual cylinders avoids a declining ratio of seed to sample as increasing dilutions are made. When dilutions are prepared directly in BOD bottles and when seeding is necessary, add seed directly to dilution water or directly to the BOD bottles.

1) Dilutions prepared in graduated cylinders-If the azide modification of the titrimetric iodometric method is used, carefully siphon dilution water, seeded if necessary, into a 1- to 2-L-capacity graduated cylinder. Fill cylinder half full without entraining air. Add desired quantity of carefully mixed sample and dilute to appropriate level with dilution water. Mix well with a plunger-type mixing rod; avoid entraining air. Siphon mixed dilution into two BOD bottles. Determine initial DO on one of these bottles. Stopper the second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, siphon dilution mixture into one BOD bottle. Determine initial DO on this bottle and replace any displaced contents with sample dilution to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C.

2) Dilutions prepared directly in BOD bottles-Using a wide tip volumetric pipet, add the desired sample volume to individual BOD bottles of known capacity. Add appropriate amounts of seed material to the individual BOD bottles or to the dilution water. Fill bottles with enough dilution water, seeded if necessary, so that insertion of stopper will displace all air, leaving no bubbles. For dilutions greater than 1: 100 make a primary dilution in a graduated cylinder before making final dilution in the bottle. When using titrimetric iodometric methods for the DO measurement, prepare two bottles at each dilution. Determine initial DO on one bottle. Stopper second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is use for DO measurement, prepare only one BOD for each dilution. Determine initial DO on this bottle and replace any displaced contents with dilution water to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C. Rinse DO electrode between determinations to prevent cross-contamination of samples.

Determination of initial DO: If the sample contains materials that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If rapid initial DO uptake is insignificant, the time period between preparing dilution and measuring initial DO is not critical.

Use the azide modification of the iodometric method or the membrane electrode method to determine initial DO on all sample dilutions, dilution water blanks, and where appropriate, seed controls.

Dilution water blank: Use a dilution water blank as a rough check on quality of unseeded dilution water and cleanliness of Incubation bottles. Together with each batch of samples incubate a bottle of unseeded dilution water. Determine initial and final DO. The DO uptake should not be more 0.2 mg/L and preferably not more than 0.1 mg/L.

Incubation: Incubate at 20°C ± 1°C BOD bottles containing desired dilutions, seed controls, dilution water blanks, and glucose-glutamic acid checks.

j. Determination of final DO: After 5 d incubation determine DO in sample dilutions, blanks, and checks

## Calculation

When dilution water is not seeded:

$$BOD_5, mg/L = \frac{D_1 - D_2}{P}$$

where:

$D_1$ = DO of diluted sample immediately after preparation, mg/L,

$D_2$= DO of diluted sample after 5 d incubation at 20'C, mg/L,

P = decimal volumetric fraction of sample used,

## A3.5.3 CHEMICAL OXYGEN DEMAND (COD)

### Introduction

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variety of samples, and case of manipulation. Oxidation of most organic compounds is 95 to 100% of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Ammonia, present either in the waste or liberated from nitrogen-containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions.

### Selection of Method

The open reflux method is suitable for a wide range of wastes where a large sample size is preferred. The closed reflux methods are more economical in the use of metallic salt reagents, but require homogenization of samples containing suspended solids to obtain reproducible results. Ampules and culture tubes with premeasured reagents are available commercially. Follow instructions furnished by the manufacturer.

## Interferences and Limitations

Volatile straight-chain aliphatic compounds are not oxidized to any appreciable extent. This failure occurs partly because volatile organics are present in the vapor space and do not come in contact with the oxidizing liquid. Straight-chain aliphatic compounds are oxidized more effectively when silver sulfate ($Ag_2SO_4$) is added as a catalyst. However, $Ag_2SO_4$ reacts with chloride, bromide, and iodide to produce precipitates that are oxidized only partially. The difficulties caused by the presence of the halides can be overcome largely, though not completely, by complexing with mercuric sulfate ($HgSO_4$) before the refluxing procedure. Although 1 g $HgSO_4$ is specified for 50 mL sample, a lesser amount may be used where sample chloride concentration is known to be less than 2000 mg/L, as long as a 10:1 ratio of $HgSO_4$:Cl - is maintained. Do not use the test for samples containing more than 2000 mg Cl -/L. Techniques designed to measure COD in saline waters are available.

Nitrite ($NO_2^-$) exerts a COD of 1.1 mg $O_2$/mg $NO_2^-$-N. Because concentrations of $NO_2^-$ in waters rarely exteed 1 or 2 mg $NO_2^-$-N /L, the interference is considered insignificant and usually is ignored. To eliminate a significant interference due to $NO_2^-$, add 10 mg sulfamic acid for each mg $NO_2^-$-N present in the sample volume used; add the same amount of sulfamic acid to the reflux vessel containing the distilled water blank.

Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively under the test conditions. For samples containing significant levels of these species, stoichiometric oxidation can be assumed from known initial concentration of the interfering species and corrections can be made to the COD value obtained.

## Sampling and Storage

Preferably collect samples in glass bottles. Test unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH<2 using conc $H_2SO_4$. Preferably acidify any sample that cannot be analyzed the same day

## General Discussion

a. Principle: Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($K_2Cr_2O_7$). The standard 2-h reflux time may be reduced if it has been shown that a shorter period yields the same results. . Colorimetric reaction vessels are sealed glass ampules or capped culture tubes. Oxygen consumed is measured against standards at 600 nm with a spectrophotometer.

b. Interferences and Limitations Volatile organic compounds are more completely oxidized in the closed system because of longer contact with the oxidant. Before each use inspect culture-tube caps for breaks in the TFE liner. Select culture-tube size for the degree of sensitivity desired. Use the 25- X 150-mm tube for samples with low COD content because a larger volume sample can be treated.

## Apparatus

a. Digestion vessels: Preferably use borosilicate culture tubes,
16- X 100-mm, 20- X 150-mm, or 25- X 150-mm, with TFE-lined screw caps. Alternatively, use borosilicate ampules, 10-mL capacity, 19- to 20-mm diam.

b. Heating block, cast aluminum, 45 to 50 mm deep, with holes sized for close fit of culture tubes or ampules.

c. Heating Block or oven, to operate at 150 ± 2°C. NOTE: Severe damage of most culture tube closures from oven digestion introduces a potential source of contamination and increases the probability of leakage. Use an oven for culture-tube digestion only when it has been determined that 2 h exposure at 150°C will not damage the caps.

d. Ampule sealer: Use only a mechanical sealer to insure strong consistent seals.

e. Spectrophotometer, for use at 600 nm with access opening adapter for ampule or 16-. 20-, or 25-mm tubes.

## Reagents

a. Digestion solution: Add to about 500 mL distilled water 10.216 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for 2 h, 167 mL conc $H_2SO_4$, and 33.3 g $HgSO_4$. Dissolve, cool to room temperature, and dilute to 1000 mL.

b. Sulfuric acid reagent: Add $Ag_2SO_4$, reagent or technical grade, crystals or powder, to conc $H_2SO_4$ at the rate of 5.5g $Ag_2SO_4$/kg $H_2SO_4$. Let stand 1 to 2 d to dissolve $Ag_2SO_4$.

c. Sulfamic acid: Required only if the interference of nitrites is to be eliminated

d. Potassium hydrogen phthalate standard: Lightly crush and then dry potassium hydrogen phthalate ($HOOCC_6H_4COOK$) to constant weight at 120°C. Dissolve 425 mg in distilled water and dilute to 1000 mL. KHP has a theoretical COD of 1.176 mg $O_2$/mg and this solution has a theoretical COD of 500 µg/mL. This solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

## Procedure

a. Treatment of samples: Measure suitable volume of sample and reagents into tube or ampule as indicated in the following table

| **Digestion Vessel** | **Sample ML** | **Digestion Solution mL** | **Sulfuric Acid Reagent ML** | **Total Final Volume mL** |
|---|---|---|---|---|
| Culture tubes: | | | | |
| 16 x 100 mm | 2.5 | 1.5 | 3.5 | 7.5 |
| 20 x 150 mm | 5.0 | 3.0 | 7.0 | 15.0 |
| 25 x 150 mm | 10.0 | 6.0 | 14.0 | 30.0 |
| Standard 10-mL ampules | 2.5 | 1.5 | 3.5 | 7.5 |

Prepare, digest, and cool samples, blank, and one or more standards as directed below

Wash culture tubes and caps with 20% $H_2SO_4$ before first use to prevent contamination. Place sample in culture tube or ampule and add digestion solution. Carefully run sulfuric acid reagent down inside of vessel so an acid layer is formed under the sample digestion solution layer. Tightly cap tubes or seal ampules, and invert each several times to mix completely. CAUTION: Wear face shield and protect hands from heat produced when contents of vessels are mixed. Mix thoroughly before applying heat to prevent local heating of vessel bottom and possible explosive reaction.

Place tubes or ampules in block digester or oven preheated to 150°C and reflux for 2 h. Cool to room temperature and place vessels in test tube rack..

b. Measurement of dichromtate reduction: Invert cooled samples, blank, and standards several times and allow solids to settle before measuring absorbance. Dislodge solids that adhere to container wall by gentle tapping and settling. Insert unopened tube or ampule through access door into light path of spectrophotometer set at 600 rim. Read absorbance and compare to calibration curve. Use optically matched culture tubes or ampules for greater sensitivity; discard scratched or blemished glassware.

c. Preparation of calibration curve: Prepare at least five standards from potassium hydrogen phthalate solution with COD equivalents from 20 to 900 mg 0,/L. Make up to volume with distilled water; use same reagent volumes, tube, or ampule size, and digestion procedure as for samples.

### Calculation

$$\text{COD as mg } O_2/L = \frac{\text{mg } O_2 \text{ in final volume} \times 1000}{\text{mL sample}}$$

## A3.7 Total Kjeldahl Nitrogen(TKN)

### General Discussion

The kjeldahl method determines nitrogen in the trinegative state. It fails to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrite, nitro, nitroso, oxime, and semi-carbazone. If ammonia nitrogen is not removed in the initial phase of the procedure, the term "kjeldahl nitrogen" is applied to the result. Should kjeldahl nitrogen and ammonia nitrogen be determined individually, "organic nitrogen" can be obtained by difference.

a. Principle: In the presence of $H_2SO_4$, potassium sulfate ($K_2S0_4$), and mercuric sulfate ($HgSO_4$) catalyst, amino nitrogen of many organic materials is converted to ammonium sulfate $[(NH_4)_2S0_4$. Free ammonia and ammonium-nitrogen also are converted to $(NH_4)_2S0_4$. During sample digestion, a mercury ammonium complex is formed and then decomposed by sodium thiosulfate ($Na_2S_2O_3$). After decomposition the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia is determined colorimetrically or by titration with a standard mineral acid.

b. Selection of ammonia measurement method: The sensitivity of calorimetric methods makes them particularly useful for determining organic nitrogen levels below 5 mg/L. The titrimetric and selective electrode methods of measuring ammonia in the distillate are suitable for determining a wide range of organic nitrogen concentrations.

## Apparatus

Digestion apparatus:

a- Kjeldahl flasks with a total capacity of 800 mL yield the best results. Digest over a heating device adjusted so that 250 mL water at an initial temperature of 25°C can be heated to a rolling boil in approximately 5 min. For testing, preheat heaters for 10 min if gas or 30 min if electric. A heating device meeting this specification should provide the temperature range of 365 to 370°C for effective digestion.

b- Distillation apparatus

c- Apparatus for ammonia determination

## Reagents

Prepare all reagents and dilutions in ammonia-free water.

a. Mercuric sulfate solution: Dissolve 8 g red mercuric oxide, HgO, in 100 mL 6N $H_2SO_4$.

b. Digestion reagent: Dissolve 134 g $K_2SO_4$ in 650 mL water and 200 mL conc $H_2S0_4$. Add, with stirring, 25 mL mercuric sulfate solution. Dilute the combined solution to 1 L with water. Keep at a temperature close to 20°C to prevent crystallization.

c. Sodium hydroxide-sodium thiosulfate reagent: Dissolve 500g NaOH and 25 g $Na_2S_2O_3.5H_20$in water and dilute to 1 L.

d. Borate buffer solution

e. Sodium hydroxide, NaOH, 6N.

## Procedure

a. Selection of sample volume and sample preparation: Place a measured volume of sample in an 800-mL kjeldahl flask.

b. Ammonia removal.. Add 25 mL borate buffer and then 6N NaOH until pH 9.5 is reached. Add a few glass beads or boiling chips and boil off 300 mL. If desired, distill this fraction and determine ammonia nitrogen. Alternately, if ammonia has been determined by the distillation method, use residue in distilling flask for organic nitrogen determination.

For sludge and sediment samples, weigh wet sample in a crucible or weighing bottle, transfer contents to a kjeldahl flask, and determine kjeldahl nitrogen. Follow a similar procedure for ammonia nitrogen and organic nitrogen determined by difference. Determinations of organic and kjeldahl nitrogen on dried sludge and sediment samples are not accurate because drying results in loss of ammonium salts. Measure dry weight of sample on a separate portion.

c. Digestion: Cool and add carefully 50mL digestion reagent (or substitute 10 mL conc $H_2SO_4$, 6.7 g $K_2SO_4$, and 1.25 mL $HgSO_4$ solution) to distillation flask. Add a few glass beads and, after mixing, heat under a hood or with suitable ejection equipment to remove acid fumes. Boil briskly until the volume is greatly reduced (to about 25 to 50 mL) and copious white fumes are observed (fumes may be dark for samples high in organic matter). Then continue to digest for an additional 30-min. As digestion continues, colored or turbid samples will turn clear or straw-colored. After digestion, let flask and contents cool, dilute to 300 mL with water, and mix. Tilt flask and carefully add 50 mL hydroxide-thiosulfate reagent to form an alkaline layer at flask bottom. Connect flask to steamed-out distillation apparatus and shake flask to insure complete mixing. A black precipitate, HgS will form, and the pH should exceed 11.0.

d. Distillation: Distill and collect 200 mL distillate below surface of 50 mL absorbent solution. Use plain boric acid solution when ammonia is to be determined by nesslerization and use indicating boric acid for a titrimetric finish. Use 50 mL 0.04N $H_2S0_4$ solution for collecting distillate for manual phenate, nesslerization, or electrode methods. Extend tip of condenser well below level of absorbent solution and do not let temperature in condenser rise above 29°C. Lower collected distillate free of contact with delivery tube and continue distillation during last 1 or 2 min to cleanse condenser.

e. Final ammonia measurement: Use the nesslerization, manual phenate, titration, or ammonia-selective electrode method

f. Blank: Carry a reagent blank through all steps of the procedure and apply necessary corrections to the results.

## Titrimetric Method

## General Discussion

The titrimetric method is used only on samples that have been carried through preliminary distillation.

## Apparatus

Distillation apparatus

## Reagents

Use ammonia-free water in making all reagents and dilutions.

a. Mixed indicator solution: Dissolve 200 mg methyl red indicator in 100 mL 95% ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in 50 mL 95% ethyl or isopropyl alcohol. Combine solutions. Prepare monthly.

b. Indicating boric acid solution: Dissolve 20 g $H_3BO_3$, in ammonia-free distilled water, add 10 mL mixed indicator solution and dilute to 1 L. Prepare monthly

c. Standard sulfuric acid titrant, 0.02N

## Procedure

a. Proceed using indicating boric acid solution as absorbent for the distillate.

b. Titrate ammonia in distillate with standard 0.02N $H_2SO_4$ titrant until indicator turns a pale lavender.

c. Blank: Carry a blank through all steps of the procedure and apply the necessary correction to the results.

## Calculation

$$\text{mg } NH_3\text{-N/L} = \frac{(A - B) \times 280}{\text{mL sample}}$$

Where:

A = volume of $H_2SO_4$ titrated for sample, ml, and

B = volume of $H_2SO_4$ titrated for blank, ml.

# A3.8 CHROMIUM

## Introduction

### Occurrence

The hexavalent chromium concentration of U. S. drinking waters has been reported to vary between 3 and 40ug/L with a mean of 3.2 ug/L. Chromium salts are used extensively in industrial processes and may enter a water supply through the discharge of wastes. Chromate compounds frequently are added to cooling water for corrosion control. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water.

### Selection of Method

Use the calorimetric method for the determination of hexavalent chromium in a natural or treated water intended to be potable. Use the electrothermal (graphite furnace) atomic absorption spectrometric method for determination of low levels of total chromium (< 50 ug/L) in water and wastewater. Use the flame atomic absorption spectrometric method or the inductively coupled plasma method to measure concentrations up milligram-per-liter levels.

### Sample Handling

If only the dissolved metal content is desired, filter sample through a 0.45-um membrane filter at the time of collection. After filtration acidify filtrate with conc nitric acid ($HNO_3$) to pH <2. If the total chromium content is desired, acidify unfiltered sample at time of collection with conc $HNO_3$ to pH <2.

### Atomic Absorption Method for Total Chromium

### Direct Air-Acetylene Flame Method

### General Discussion

This method is applicable to the determination of antimony, cobalt, bismuth, cadmium, calcium, cesium, chromium, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc.

## Apparatus

Atomic absorption spectrometer.

## Reagents

a. Air, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.

b. Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa (100 psi) acetylene.

c. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in, the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (NOTE: If the source water contains Hg or other volatile metals, single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water.

d. Calcium solution: Dissolve 630 mg calcium carbonate, $CaCO_3$, in 50 mL of 1 + 5 HCl. If necessary, boil gently to obtain complete solution. Cool and dilute to 1000 mL with water.

e. Hydrochloric acid, HCl, 1%, 10%, 20%, 1 + 5, 1 + 1, and conc.

f. Lanthanum solution: Dissolve 58.65 g lanthanum oxide, $La_2O_3$,, in 250 mL conc HCl. Add acid slowly until the material is dissolved and dilute to 1000 mL with water.

g. Hydrogen peroxide, 30%.

h. Nitric acid, HNO,, 2%, 1 + 1, and conc.

i. Aqua regia: Add 3 volumes conc HCl to 1 volume conc $HNO_3$.

j. Standard metal solutions: Prepare a series of standard metal solutions in the optimum concentration range by appropriate dilution of the following stock metal solutions with water containing 1.5 mL conc $HNO_3$/L. Thoroughly dry reagents before use. In general, use reagents of the highest purity. For hydrates, use fresh reagents.

k. Chromium: Dissolve 0.1923 g $CrO_3$ in water. When solution is complete, acidify with 10 mL conc $HNO_3$, and dilute to 1000 mL with water; 1.00 mL = 100 ug Cr.

## Procedure

a. Sample preparation: Required sample preparation depends on need to measure dissolved metals only or total metals.

b. Instrument operation: Because of differences between makes and models of atomic absorption spectrometers, it is not possible to formulate instructions applicable to every instrument. See manufacturer's operating manual. In general, proceed according, to the following: Install a hollow-cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to Tables. Set slit width according to manufacturer's suggested setting for the element being, measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Readjust current as necessary after warm up. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Let flame stabilize for a few minutes. Aspirate a blank consisting of either deionized water or an acid solution containing the same concentration of acid in standards and samples. Zero the instrument. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Adjust burner both vertically and horizontally to obtain maximum response. Aspirate blank again and rezero the instrument. Aspirate a standard near the middle of the linear range. Record absorbance of this standard when freshly prepared and with a new hollow-cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow-cathode lamp and standard.

The instrument now is ready to operate. When analyses are finished, extinguish flame by turning off first acetylene and then air.

c. Standardization: Select at least three concentrations of each standard metal solution to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting, on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer.

d. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc $HNO_3$/L. Atomize blank and zero instrument. Atomize sample and determine its absorbance.

## A3.9 OIL AND GREASE'

### Introduction

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, groups of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in an organic extracting solvent. "Oil and grease" is defined as any material recovered as a substance soluble in the solvent. It includes other material extracted by the solvent from an acidified sample (such as sulfur compounds, certain organic dyes, and chlorophyll) and not volatilized during the test. Petroleum ether is used as the solvent for natural and treated waters and n-hexane for polluted waters. Trichlorotrifluoroethane is considered as an optional solvent for all sample types. However, because of environmental problems associated with chlorofluorocarbons, an alternative solvent (80% n-hexane and 20% methyl-tert-butyl ether) is included for gravimetric methods. This alternative solvent mixture produces results very similar to those obtained on the same samples with trichlorotrifluoroethane. Solvent-recovery techniques have been included and solvent recycling is strongly recommended.

It is important to understand that, unlike some constituents that represent distinct chemical elements, ions, compounds, or groups of compounds, oils and greases are defined by the method used for their determination.

The methods presented here are suitable for biological lipids and mineral hydrocarbons. They also may be suitable for most industrial wastewaters or treated effluents containing these materials, although sample complexity may result in either low or high results because of lack of analytical specificity. The method is not applicable to measurement of low-boiling fractions that volatilize at temperatures below 70'C when trichlorotrifluoroethane is used or below 85°C when the n-hexane/methyl-tert:butyl -ether solvent mix is used.

### Significance

Certain constituents measured by the oil and grease analysis may influence wastewater treatment systems. If present in excessive amounts, they may interfere with aerobic and anaerobic biological processes and lead to decreased wastewater treatment efficiency. When discharged in wastewater or treated effluents, they may cause surface films and shoreline deposits leading to environmental degradation.

A knowledge of the quantity of oil and grease present is helpful in proper design and operation of wastewater treatment systems and also may call attention to certain treatment difficulties

In the absence of specially modified industrial products, oil and grease is composed primarily of fatty matter from animal and vegetable sources and from hydrocarbons of petroleum origin. A knowledge of the relative composition of a sample minimizes the difficulty in determining the major source of the material and simplifies the correction of oil and grease problems in wastewater treatment plant operation and stream pollution abatement.

## Selection of Method

For liquid samples: the partition-gravimetric method is used

## Sample Collection, Preservation, and Storage

Collect a representative sample in a wide-mouth glass bottle that has been washed with soap, rinsed with water, and finally rinsed with solvent to remove any residues that might interfere with the analysis. Collect a separate sample for an oil and grease determination. Do not overfill the sample container, and do not subdivide the sample in the laboratory. If analysis is to be delayed for more than 2 h, acidify to pH 2 or lower with 1: 1 HCI and refrigerate. When information is required about average grease concentration over an extended period, examine individual portions collected at prescribed time intervals to eliminate losses of grease on sampling equipment during collection of a composite - sample.

In sampling sludges, take every possible precaution to obtain a representative sample. When analysis cannot be made within 2 h, preserve samples with 1 mL conc HCI/80 g sample and refrigerate. Never preserve samples with CHCI, or sodium benzoate.

## Partition-Gravimetric Method

## General Discussion

Dissolved or emulsified oil and grease is extracted from water by intimate contact with an extracting solvent. Some extractables, especially unsaturated fats and fatty acids, oxidize readily; hence, special precautions regarding temperature, and solvent vapor displacement are included to minimize this effect. Organic solvents shaken with some samples may form an emulsion that is very difficult to break. This method includes a means for handling such emulsions. Recovery of trichlorotrifluoroethane and other solvents is discussed; recovery can reduce both vapor emissions to the atmosphere and costs of solvent supply.

## Apparatus

a. Separatory funnel, 2-L, with TFE* stopcock.

b. Distilling flask, 125-mL.

c. Liquid funnel, glass.

d. Filter paper, 11-cm diam.t

e. Centri ge, capable of spinning at least four 100-mL glass
centrifuge tubes at 2400 rpm or more.

f. Centrifuge tubes, 100-mL, glass.

g. Water bath, capable of maintaining 85'C.

h. Vacuum pump or other source of vacuum.

i. Distilling adapter with drip tip. Setup of distillate recovery
apparatus is shown in Figure 5520:1. Alternatively, use cornmerci,ally available solvent recovery equipment.

j. Ice bath.

k. Waste receptacle, for used solvent.

1. Desiccator.

## Reagents

a. Hydrochloric acid, HCI, 1 + 1.

b. Trichlorotrifluoroethane (1,1,2-trichloro-1,2,2-trifluoro-
ethane), boiling point 47'C. The solvent should leave no measurable residue on evaporation; distill if necessary. Do not use any plastic tubing to transfer solvent between containers.

c. n-Hexane, boiling point 69'C. The solvent should leave no measurable residue on evaporation; distill if necessary. Do not yse any plastic tubing to transfer solvent between containers.

d. Methyl-tert-butyl ether, boiling point 55'C to 56'C. The solvent should leave no measurable residue on evaporation; distill if necessary. Do not use any plastic tubing to transfer solvent between containers.

e. Sodium sulfate, Na,SO,, anhydrous crystal.

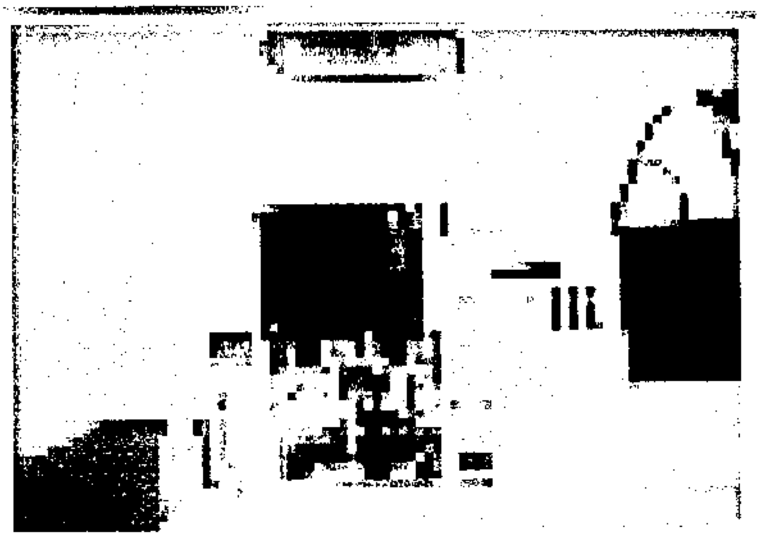
## Procedure

When a sample is brought into the laboratory, mark sample level on bottle for later determination of sample volume. Acidify with 1:1 HCl to pH 2 or lower (generally, 5 mL is sufficient). Transfer sample to a separatory funnel. Carefully rinse sample bottle with 30 mL of extracting solvent and add solvent washings to separatory funnel. Shake vigorously for 2 min. Let layers separate. Next, depending on the solvent used (n-hexane/methyltert-butyl ether will be upper layer or trichlorotrifluoroethane ill be lower layer) drain solvent layer through a funnel containing a filter paper and 10 g $Na_2SO_4$, both of which have been solvent-rinsed, into a clean, tared distilling flask. If a clear solvent layer cannot be obtained and an emulsion of more than about 5 mL exists, drain emulsion and solvent layers into a glass centrifuge tube and centrifuge for 5 min at approximately 2400 rpm. Transfer centrifuged material to an appropriate separatory funnel and drain solvent layer through a funnel with a filter paper and 10 g $Na_2SO_4$, both of which have been prerinsed, into 'a clean, tared distilling flask. Recombine aqueous layers and any remaining emulsion or solids in separatory funnel. For samples with <5 mL of emulsion, drain only the clear solvent through a' funnel with pre-moistened filter paper and 10 g $Na_2S0_4$. Recombine aqueous layers and any remaining emulsion or solids in separatory funnel. Extract twice more with 30 mL solvent each time, but first rinse sample container with each solvent portion. Repeat centrifugation step if emulsion persists in subsequent extraction steps. Combine extracts in tared distilling flask, and include in flask a final rinsing of filter and $Na_2SO_4$ with an additional 10 to 20 mL solvent. Distill solvent from flask in a water bath at 70'C for trichlorotrifluoroethane or 85'C for the n-hexane/methyl-tert-butyl ether mixture. To maximize solvent recovery, fit distillation flask with a distillation adapter equipped with a drip tip and collect solvent in an ice bath-cooled receiver. When visible solvent condensation stops, remove flask from water bath. Cover water ' bath and drv flasks on top of cover at 70'C for trichlorotrifluoroethane or 85'C for the nhexane/methyl-tert-butyl ether mixture for 15 min. Draw air through flask with an

Container in which removal of chromium experiment was carried out (tannery)

Samples taken before and after the experiment of chromium removal

- On the left: before the removal, chromium content is about 5000mg/L
- On the right: after the removal, chromium content is less than 1mg/L



The Atomic Absorption Spectrophotometer used for the analysis of chromium

# Appendix Five

## Safety Data Sheet
## For
## Chromium

# Safety Data Sheet

CHROMIUM TRIOXIDE

Chromic acid; chromic anhydride; $CrO_3$

## Physical Properties

| | |
|---|---|
| Boiling point °C | 250 |
| Melting point °C | 197 |
| Relative density (water=1) | 2.7 |
| Solubility in water | reaction |
| Relative molecular mass | 100.0 |
| MAC in mg/m$^3$ (As chromium) | 0.05 |

## Other Characteristics

VIOLET TO RED CRYSTALS

The substance decomposes upon heating above 250°, forming chromium III oxide ($Cr_2O_3$) and oxygen, which increases fire hazard. The substance is a strong oxidant. When it is dissolved in water, it is a strong acid, reacts violently with bases and is corrosive. Reacts violently with reducing materials, causing fire and explosion hazards. The substance may be absorbed into the body by inhalation and ingestion. The substance is corrosive to the eyes, the skin and the respiratory tract. Kidney injury may occur. Inhalation of the substance may cause lung oedema***. Intensive contact with skin may cause dermatitis.

## Hazards/Symptoms

**Fire:** not combustible, many reactions may cause fire and explosion

**Inhalation:** pungent, sore throat, coughing, shortness of breath, laboured breathing

**Skin:** corrosive, redness, pain, blurred vision

**Ingestion:** corrosive, sore throat, abdominal spasm, vomiting, diarrhoea

## Prevention

1. No contact with combustible substances
2. Local exhaust or breathing protection
3. Protective gloves, protective clothing

4. Face shield or eye protection in combination with breathing protection
5. Do not eat, drink of smoke during work

## Fire Extinguishing Agent/First Aid

1. Fresh air, rest, half upright Position, and transport to hospital
2. Remove contaminated clothes, rinse skin with plenty of water or shower and send to a doctor
3. Rinse with plenty of water, then transport to a doctor
4. Rinse mouth, give plenty of water to drink, and transport to hospital immediately

## Spillage

Sweep up spilled substance, carefully collect remainder, (extra personal protection: class 2b particle filter respirator)

## Storage

Separated from combustible substances and reducing gents, dry

## Packaging & Labelling

Special material

UN: 1463

R: 8-35

S: 28

**Notes**

Depending on the degree Of exposure, periodical medical examination is desirable.

***The symptom of lung oedema often do not become manifest until a few hours have passed, and they are aggravated by physical effort. Rest and hospitalization are therefore essential. Before this manifestation, administration of a corticosteroid-containing spray, by a doctor or a person authorized by him or her, should be considered.

**Reference**

Handling chemicals safely, 1980, (Dutch association of safety experts, Dutch chemical industry association, Dutch safety institute)

# Appendix Six

## Questionnaire

# FORM OF QUESTIONNAIRE

ame of Tannery:------------------------------------------------
ty:-------------------------------------------- Tel. No. ---------------------
wner:--------------------------------------------------------
ducational level :------------------------------------------------

## 1 general information

ge of the factory ------------ years
ea of the tannery ----------- m2
umber of workers

umber of hides processed per day Kg/day hides/day
umbe of working hours per day
umber of working days per week
cation industrial commercial residential others
if located in resedential area what is the nearest residence

## 2 Process Description

Process Description (stages)

☐ salting with food salt
☐ washing
☐ hair removal by using sodium sulfide and lime
☐ washing
☐ fat removal by using special soap and chemical fertilizer
☐ addition of special enzymes for fat extraction from the hide
☐ washing
☐ pickling by using sulfuric and formic acid
☐ soaking in chrome solution
☐ releif of thickness
☐ soaking in oils
☐ dying
☐ finishing

## 3 Water Consumption

mount of water consumed

per day
per 100 hide
per 100kg

## 4 Pretreatment and disposal methods

xistence of pretreatment technique on site
yes if yes what is the method of treatment
no if no why
sposal of liquid wastes into sewage system else? how:

mount of liquid wastes produced per day
isposal of solid wastes containers No?
mount of solid wastes produced per day
ype of solid wastes produced per day

## 5 Quality Control

efore disposing the effluent are there any samples taken for analysis
o
es
yes who asked for this analysis

by the tannery owner
by authotity which authority

## 6 Safety Procedures

o workers use gloves yes no
o workers use special clothes yes no
/here they take food and rest
inside outside inside but in separate room
ny injury happened inside the tannery no yes? why
ealth problems inside the tannery no yes? like what
espiratory problems no yes if yes when
ote the existence of any kind of ventilation
Natural
Mechanical
Where

## actory Environment

7 note the floor surface

good conditions
bad conditions

8 note the odour

9 note how workers deal with chemicals

Is there any person responsible for the chemicals

10 existence of plants around no yes? from where irrigated
existence of animals around near far

| | Educational level | | | | | |
|---|---|---|---|---|---|---|
| orker | none | elem | prep | sec | else | health remarks |
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| 20 | | | | | | |

aw materials used in the production process

| o. | chemical used<br>chemical name,formula,commercial name,UN No,CAS No | purpose of use | quantity |
|---|---|---|---|
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# Appendix Seven

## Manuals

# Atomic Absorption Spectrophotometer

## PERKIN ELMER
## AAnalyst 100

**Standard Atomic Absorption Conditions for Cr**

| Wavelength (nm) | Slit (nm) | Relative Noise | Characteristic Concentration (mg/L) | Characteristic Concentration Check (mg/L) | Linear Range (mg/L) |
|---|---|---|---|---|---|
| 357.9 | 0.7 | 1.0 | 0.078 | 4.0 | 5.0 |
| 359.4 | 0.7 | 1.2 | 0.10 | 5.0 | 7.0 |
| 360.5 | 0.7 | 7.7 | 0.14 | 7.0 | 7.0 |
| 425.4 | 0.7 | 8.8 | 0.20 | 12.0 | 7.0 |
| 427.5 | 0.7 | 10.0 | 0.27 | 15.0 | 7.0 |
| 429.0 | 0.7 | 6.9 | 0.38 | 20.0 | 5.0 |

Recommended Flame: air-acetylene, reducing (rich, yellow)
Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity Nebulizer or impact bead will typically provide a 2-3 x sensitivity improvement.
Characteristic Concentration with a $N_2O$-$C_2H_2$ flame at 357.9 nm: 0.31 mg/L

**Standard Flame Emission Conditions for Cr**

| Wavelength (nm) | Slit (nm) | Flame |
|---|---|---|
| 425.4 | 0.2 | Nitrous oxide-acetylene |

**Stock Standard Solution**

CHROMIUM, 1000 mg/l stock: Dissolve 3.735 g of potassium chromate, $K_2CrO_4$, in deionized water and dilute to 1 liter with deionized water.

**Flames**

The determination of chromium requires a fuel-rich (yellow) air-acetylene flame. The absorption is sensitive to the fuel-to-air ratio. The nitrous oxide-acetylene flame reduces or eliminates many chemical interferences, but sensitivity is reduced.

**Interferences**

Chromium absorption is suppressed in the air-acetylene flame by the presence of iron and nickel. If the analysis is performed in a lean flame, the interference can be lessened but the sensitivity will be reduced. The addition of 2% ammonium chloride ($NH_4Cl$) to sample and standard solutions controls the interference caused by iron. An excess of phosphate will depress the chromium response and can be overcome by the addition of calcium. Cr (VI) and Cr (III) exhibit different sensitivities. It is recommended that if Cr (III) is present, it be oxidized to give Cr (VI).

# pH/mV/Temperature METER

## EC10 PORTABLE
## HACH COMPANY
## MODEL 50050

SPECIFICATIONS

**pH range: -2.00 to 19.99**

| | |
|---|---|
| Resolution | 0.01 |
| Relative accuracy | ±0.02 |
| Good slope range | 45 to 70 mV/decade |

**Millivolt range: -1600.0 to +1600.0**

| | |
|---|---|
| Resolution | 0.1 mv |
| Relative accuracy | ±0.2 mV or ±0.05% of AE whichever is greater |

**Temperature range : -5.0 to 105.0 'C**

| | |
|---|---|
| Resolution | 0. 1 °C |
| Relative accuracy | ±1.0 °C |

**Display:** **Custom LCD**

**Inputs: BNC, pin tip, DIN, power**

**Power requirements:**
9 volt alkaline battery
-or-
9 VDC line adapter (battery eliminator)
115V, 60 Hz - North American Style Plug
23OV, 50 Hz - Continental European Style Plug

**Input impedance**
$>10^{12}$ ohms

**Instrument drift**
<50 microvolts/°C

**Input bias current**
< + 1 picoamp at 25 °C and < + 4 picoamps over full operating range

**Environmental requirements**
5 to 45 °C and 5 to 85% relative humidity, non-condensing

**Meter dimensions**
8 x 3.3 x 2 inches (20 x 8 x 5 cm)

**Case**
Dust and Splash Resistant, Chemical Resistant

# Conductivity Meter

## C0150 Conductivity Meter
## HACH COMPANY
## Model 50150

SPECIFICATIONS

**Conductivity:**

| | |
|---|---|
| Measurement Range | 0 to 199,900 µS |
| Range 1 | 0 to 199.9 µS |
| Range 2 | 200 to 1999 µS |
| Range 3 | 2.00 to 19.99 mS |
| Range 4 | 20.0 to 199.9 mS |
| Accuracy | ±0.5% of full scale of reading within each range, maximum |
| Cell Constant Range | 0.07 to 14.99 |
| Cell Constant Resolution | 0.0700, 1.000, 10.00 |

**Salinity:**

| | |
|---|---|
| Measurement Range | 0.0 to 80.0 ppt |
| Resolution | 0.1% |
| Accuracy | ±0. 1 %, (0 to 35 °C, 0 to 42%) |

**Total Dissolved Solids:**

| | |
|---|---|
| Measurement Range | 0 to 19900 mg/L |
| Accuracy | ±1% RSD, 5 to 70 °C |
| Resolution | 3 significant digits |
| Calibration | in Conductivity Mode |

**Temperature Measurement:**

| | |
|---|---|
| Range | -10.0 to 110.0 °C |
| Relative Accuracy | ±1.0 °C |
| Resolution | 0.1 °C |

**Temperature Compensation (Automatic or Manual):**

| | |
|---|---|
| Range | -10.0 to 110.0 °C |
| Coefficient | 2.1 % per degree C |
| Reference Temperature | 20 or 25 °C |

**Reference Temperature:**

20 or 25 °C, selectable

**Display:** Custom LCD

**Inputs:** 8 pin DIN, RS232, Power

**Outputs**: RS232

**Power Requirements:**
One 9V Alkaline Battery
or
9 VDC line adapter (battery eliminator)
115V, 60 Hz - North American Plug
23OV, 50 Hz - Continental European Plug

**Environmental Requirements:**

| | |
|---|---|
| Operating | 5 to 45 °C and 5 to 85% relative humidity, non-condensing |
| Storage | -20 to 60 °C and 5 to 85% relative Humidity, non-condensing |

**Meter Dimensions:**
8 x 3.3 x 1.9 inches (20.5 x 8.3 x 4.8 cm)

**Case:** 1P54 and Chemical Resistant

**Data Logging:**
50 data set storage
Display output
RS232 output

**Conductivity Probe Specifications**

| Model | Cable Length | Cell Constant | Minimum Range |
|---|---|---|---|
| 50160 | 1.0 m | 0.1 (±20%) | 0.1 μS - 100μS |
| 50161 | 1.0 m | 1.0 (±10%) | 1.0 μS - 100 mS |
| 50162 | 3.0 M | 1.0 (±1 0%) | 1.0 μS - 100 mS |