



#### **OCCASION**

This publication has been made available to the public on the occasion of the 50<sup>th</sup> anniversary of the United Nations Industrial Development Organisation.



#### **DISCLAIMER**

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

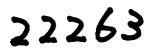
#### FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

#### **CONTACT**

Please contact <u>publications@unido.org</u> for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org





# UNIDO Contract N. 95/230/P

Project US/CPR/92/120



## ASSISTANCE IN POLLUTION CONTROL AND TREATMENT OF TANNERY WASTES IN SELECTED AREAS OF CHINA

## FINAL REPORT

Project Manager

Jakov Buljan,

Agro-Industries and Sectoral Support Branch

#### Main used abbreviations:

BOD<sub>5</sub> (or BOD): Biochemical Oxygen Demand, 5 days (Winkler method)
COD: Chemical Oxygen Demand (dichromate reflux method)

Cr III : Trivalent Chromium
DO : Dissolved Oxygen

DS : Dry Solids d.w. : dry weight

ETP : Effluent Treatment Plant m³ : cubic meter (1000 litres) mg/L : milligrams per litre

max. : maximum min. : minimum

N-NH<sub>3</sub> : Ammonia Nitrogen

MLSS : Mixed Liquor Suspended Solids

MLVSS : Mixed Liquor Volatile Suspended Solids

O&G: oil and grease

PAC : Poly-Aluminium Chloride

S2- : Sulphide (as S)
SS : Suspended Solids
tot. Cr : Total Chromium
w.s.w. : wet salted weight

#### **Local Currency**

RMB (Yuan) Ren Min Bi: 1 US \$ = 8.8 RMB ca. (February 1999)

#### **Abstract**

The report summarises the most relevant activities of the Subcontractor's team in the period between 1996 and 1998 and the main achieved results in execution of the contract N. 95/230P between UNIDO and STUDIO TECNICO dr. G. Clonfero of 22 January 1996.

#### LIST OF CONTENTS

1. SUMMARY OF THE ACTIVITY AND SERVICES PROVIDED	Page 3
2. OVERALL ACHIEVED RESULTS	Page 6
3. SITUATION BEFORE AND AFTER THE INTERVENTIONS	
AT EACH PROJECT SITE (historical)	Page 8
3.1 THE P.L.A. FACTORY N° 3513 - XIAN TANNERY	Page 8
3.2 JANGSU NANJING TANNERY	Page 11
3.3 DA CHANG COMPLEX (SHANGHAI RICHINA LEATHER Co.)	Page 15
4. LEGISLATION SURVEY	Page 22

#### **ANNEXES**

ANNEX 1: REPORTS AND MANUALS

ANNEX 2: MISSIONS TO THE PROJECT SITES

ANNEX 3: MEETINGS AT UNIDO HEADQUARTERS

#### 1. SUMMARY OF THE ACTIVITY AND SERVICES PROVIDED

The execution of the contract has been accomplished in four successive phases:

#### Phase I (preparatory phase)

The subcontractor's team activity of this phase was mainly focused on the following issues:

- data collection: production capacity, leather processing procedures, raw materials, water consumption, chemicals used, etc.
- estimate of the total expected volume of waste water (current and future) and quantity of the produced sludges, and pollution loads.
- other relevant local information for the preparation of the techno-economic ETP rehabilitation study: environmental regulations for discharge of industrial effluents and solid wastes disposal, evaluation of the possible secondary environmental impacts, etc.).
- on-site investigation of the existing processes, equipment and facilities for effluent and solid treatment, their effectiveness, possible problems and limits. Assessment of the reliability of the in-plant and laboratory monitoring apparatuses and methods.
- -specifically for Da Chang- investigation and optimisation of the present sludge conditioning and dewatering process. Preparation of a basic design of an on-site system for the temporary disposal/storage of the dewatered sludge.
- assessment, update and consolidation of the information contained in the reports already available for the three project sites, and specifically:
- "Field Mission to Shanghai Leather Corporation, Da Chang Complex and ETP and Nanjing Tannery and ETP", Mr. Madlen Bosnic, expert in tannery effluent treatment equipment, UNIDO consultant -January 1995
- 2. "Nanjing Tannery Effluent Treatment Plant", Ms. Song Xian Wen, Shanghai Leather Technology Centre July 1994
- "Environmental Protection Training Plan for Leather Industry, 1995-1996", China Leather Industry Research Institute, Beijing - February 1995
- 4. "List of Instruments and Equipment for Training Plan of Leather Environmental Protection", China Leather Industry Research Institute, Beijing February 1995
- 5. "Treatment of Tannery Effluent of Xian Leather & Shoe-making Factory", Ms. Meng Qingyuan, CLIA February 1995
- 6. "Chrome Management in Xian Tannery", Mr. A.D. Covington, expert in treatment of tannery waste (chrome management), UNIDO consultant September 1995.
- 7. "Treatment for Industrial Pollution in Xian Leather and Shoes Factory", Xian Leather & Shoe-making Factory April 1995.

#### Phase II (design)

Main subcontractor's team activity:

- Preparation of specific techno-economic study for upgrading and optimisation of the ETP at each project site, containing:
  - i. detailed design of the rehabilitation interventions supported by calculations, and flow-diagrams of the original and rehabilitated plant, and drawings of the civil works.
  - ii. justification of the proposed rehabilitation interventions, expected pollution reduction and/or advantages for operation and maintenance.
  - iii. specification of the equipment needed, additional laboratory apparatuses for effluent analysis and plant monitoring, and recommended spare parts for both the existing and new equipment.

#### Phase III (implementation of the rehabilitation interventions)

Main subcontractor's team activity:

- Assistance in the preparation of the UNIDO tender documents (requests for proposal) for the acquisition of the equipment and spare parts for rehabilitating the ETPs, and in the technical evaluation of the obtained proposals.
- Contacts with the selected suppliers for technical questions and supplementary details about equipment installation.
- Preparation of the drawings of the necessary modifications of the existing civil works for accommodating the new equipment (specifically for Xian Tannery and Da Chang).
- Technical guidance to factories in the course of installation and commissioning of the new equipment.

#### Phase IV (plant' start up and on site training)

Main subcontractor's team activity:

- Assistance in the trial run, commissioning and optimisation of the modified ETPs with the view of producing the effluent that satisfies the local discharge standards.
- Theoretical and practical training of personnel in charge of the ETP operation and control.
- Assistance in conducting appropriate laboratory control to monitor plants' performance/efficiency and upon stabilisation of the modified treatment systems prepare action and monitoring manual for each effluent
- training through both practical (in-plant and laboratory) activities and theoretical discussions.

The training has been mainly focused on:

- plant operation and maintenance,
- treatment process step tuning and troubleshooting,
- tannery effluent and solid waste analysis,
- routine methods and procedures of plant monitoring and control.

The list of the Reports and Manual prepared by STUDIO TECNICO, and the missions to the project sites of the Subcontractor's team are reported in Annex.

#### 2. OVERALL ACHIEVED RESULTS

- Following critical assessment, design and equipment specifications for each (C)ETP site was prepared.
- Information about discharge standards legislation has been collected.
- The equipment provided through the project is installed and in operation. Minor problems encountered during the commissioning have been successively resolved.
- Two of the three ETPs are fully rehabilitated and in operation, (only For Nanjing Tannery, because of the mentioned past problems, part of the planned interventions must be still implemented).
- The characteristics of the final treated effluent are also highly improved, the final effluent of the three ETPs comply with the national discharge standards (only at Da Chang some difficulty still persists for obtaining a regular conformity for the Ammonia Nitrogen parameter).
- The on-plant training is successfully concluded: the effluent staff at the three project sites
  has reached adequate self-confidence in the ETP operation and maintenance, and the
  laboratory staff exhibits typical ability in routine procedures and methods for effluent
  analysis.
- The capability level of the laboratory staff is sufficient for routine effluent monitoring.
- Apart from some difference at the three project sites, the effluent laboratories are adequately equipped for the routine analyses and controls. Some more complex analyses are demanded to external laboratories.
- An appropriate and realistic plant monitoring program has been prepared and in use at the three project sites: commonly equalisation, primary sedimentation/flotation, secondary sedimentation and final effluent after tertiary treatment if implemented or utilised) and one sample of the biological aeration tank are daily analysed. COD, Chromium, Ammonia Nitrogen (specifically at Da Chang), Sulphide, SS and DO, plus MLSS and MLVSS of the biological aeration tank, and DS of dewatered sludge are the daily controlled parameters. Once per week BOD of the final effluent, and Chromium content of the sludge are also tested.
- The performances of sludge treatment units are also satisfactory: DS of the dewatered sludge habitually overcome 30% and filtration cycles are routinely performed.

# 3. SITUATION BEFORE AND AFTER THE INTERVENTIONS AT EACH PROJECT SITE (historical)

#### 3.1 THE P.L.A. FACTORY N° 3513 - XIAN TANNERY

The factory combines three industrial activities: leather processing, shoe-making and felt-production.

Tannery processing: bovine hides from raw to finished upper leather (chrome tanning), buffalo hides from raw to sole leather (vegetable tanning), and sheep skins from raw to lining. All wastewaters produced by the factory are, after treatment, discharged into the municipal sewer.

#### 3.1.1 Chrome recovery plant (direct recirculation)

The adopted system is simple and inexpensive, the spent tanning liquors from the cattle hides are segregated and recycled after filtration and settling. The unit consists of six successive mesh screens and two parallel barriers of stones of 4-6 cm size and a series of five interconnected tanks in which solids sedimentation occurs.

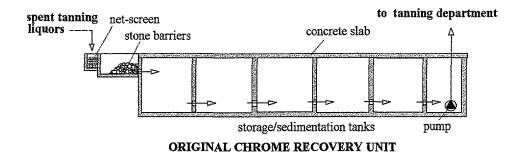
The settled liquor is reused in the preparation of the new tanning float.

The recovery process is limited to the cattle hides tanning: 75-80% of the spent tanning liquors is recycled and the remaining discharged to the ETP.

The system is able to guarantees enough constant characteristics of the recycled liquor and does not affect negatively the quality of the produced leather.

#### Detected problems (p) and adopted ameliorating interventions (i)

- Ineffective and labour intensive system (net-screens and stone barriers) for the filtration of the Chrome liquors. During the manual cleaning operation, an important part of the trapped materials crosses the barrier and solids settle in the storage tanks causing abundant deposits and frequent laborious cleaning operations.
- i A more effective screening system has been implemented consisting of a mechanised screen (local) and a fine screen (imported) (see following sketch).



mechanised screen

spent tanning
liquors

pump

pre-storage/pumping

storage/sedimentation tanks pump

MODIFIED CHROME RECOVERY UNIT

#### 3.1.2 Effluent Treatment plant

Brief description of the original ETP (see flow diagram No. 1 attached)

The factory's waste waters (i.e. from cattle and buffalo hides, sheep skins and felt processing) are mixed in one main channel connected to the ETP.

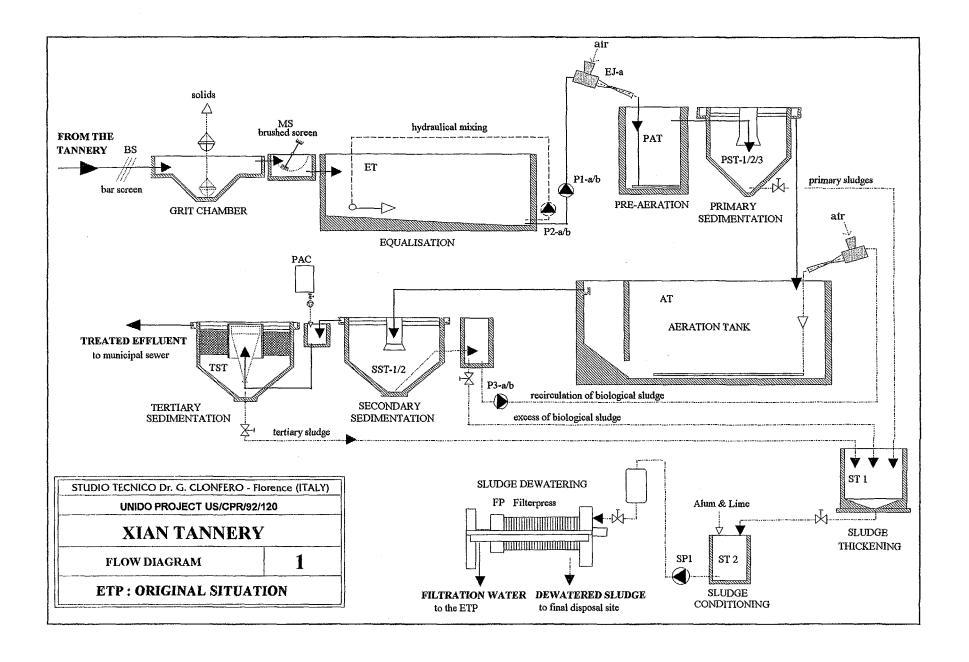
The effluent after coarse screening (bar screen BS), is pre-settled in a grit chamber and, after a second screening (brushed screen MS) flows by gravity into the equalisation tank (ET).

In the original design the equalisation tank was mixed by pumping, recirculation and injection of the same effluent (hydraulic mixing). Two pumps (P2 -a/b) and a series of pipes and nozzles were installed for this service, but the system was successively abandoned because of its poor efficiency and performance. The piping is now completely destroyed by corrosion and clogged by solids.

The effluent is transferred (centrifugal pump P1) to the pre-aeration tank (PAT). The same pumped effluent operates the "Jet aeration" (EJ-a).

The effluent flows by gravity into three parallel primary sedimentation tank type Dortmund (PST 1/2/3). No flocculation by dosage of chemicals (coagulants) is performed at this stage.

The settled effluent enter the biological aeration tank (AT). Also in this case the aeration/mixing is realised by two "Jet aerators" (EJ-b/c). Another aerator is a stand-by unit.



The recirculation of the biological sludge from the secondary sedimentation is operating the "Jet aerators". The mixed liquor of the aeration tank enter a stationary section (separated by a baffle wall) where part of the biological sludge settles and returns to the mixing/aeration section. The overflow is transferred (by gravity) to two parallel secondary sedimentation tanks (SST-1/2).

The settled sludge is continuously recirculated to the aeration tank (centrifugal pumps P3-a/b) through EJ-b/c and the supernatant flows to the tertiary treatment.

The tertiary treatment consists of a dosage of Poly-aluminium Chloride (PAC) followed by a final sedimentation in TST. The tertiary treatment is only seldom used, when the values of suspended solids and COD are above the discharge limits.

The material from the grit chambers is periodically removed by means of a mechanic bucket and transported to the disposal site as a slurry.

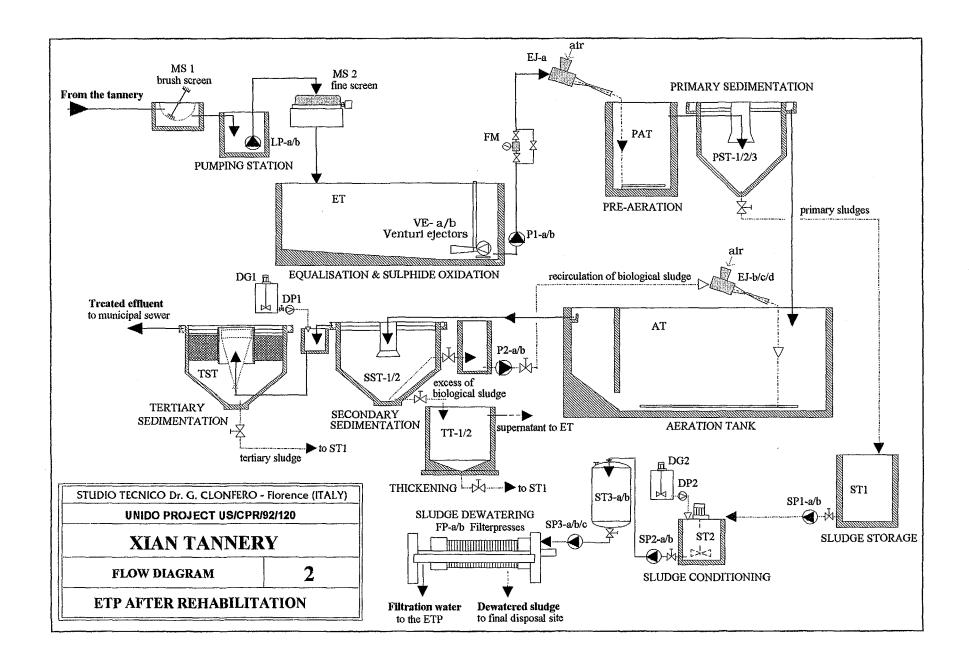
The sludges from the primary sedimentation tanks, the surplus sludges from the biological treatment and the possible chemical sludge from tertiary sedimentation are jointed together in the thickening tank (ST1) and successively dewatered by filter press (FP). A sludge conditioning tank (ST2) is installed before the mechanical dewatering where dosing of Lime and PAC is possible. At the present no chemical conditioning is done.

The filtration water is piped back to the ETP.

#### Detected problems (p) and taken ameliorating interventions (i)

- p High water consumption in the tannery department. The water consumption for the leather processing (80-100 L/kg of wet salted weight) is two times that of the Chinese standard GB 8978-88 indicating a max. permitted water consumption of 50 L/kg wet salted weight, and 3 times that commonly used in the European tanneries.
- i Proper monitoring of the water consumption through the installation of a series of flowmetering devices, and more rational and careful water use (batch washing, short floats, etc.),
- p The grit chamber is useless and troubling. There are not significant quantities of grit/sand in the effluent: the deposit is mainly constituted of particulate materials (hairs, fleshings, plastics, etc.) and other settleable solids (mostly lime). Such a residue was containing colloidal materials very difficult to be dewatered. Furthermore the system causes flies, bad smell and a very anaesthetic and unpleasant impact.
- i Elimination of the grit chamber. Conversion of the tank into a pumping station, two submersible pumps, LP-a/b (imported), and implementation of a mechanised fine screen, MS 2 (imported).
- Absence of mixing in the equalisation tank causing abundant solids deposits and frequent cleaning operations. Because of underground constructed and covered by a concrete slab, the removal of the settled material from the equalisation tank is very difficult and high hazardous for the workers.
- i Implementation of a proper mixing and aeration system in equalisation. Two Venturi ejectors, VE-a/b (imported), have been installed in the equalisation tank.

- p Insufficient capacity of the sludge dewatering unit.
- i Installation of two new recessed plate filter presses of bigger capacity, FP-a/b (local).
- p Lack of on-line instrumentation for the control and monitoring of the effluent flow.
- i Installation of one on-line magnetic flow-meter, FM, (imported) for the monitoring and recording the treated flow.
- p Insufficient in-plant monitoring and control.
- i One portable dissolved Oxygen meter and one pH-meter for laboratory and on field measurements has been supplied.



#### 3.2 JANGSU NANJING TANNERY

The tannery processes pig and goat skins from raw to finish (chrome tanning). After treatment, the effluent is discharged into the municipal sewer.

#### **3.2.1 CHROME RECOVERY** (by precipitation and mechanical dewatering)

The original Chrome recovery plant had been designed by national experts. Successively the original process and operation procedure has been upgraded through the technical assistance of the project US/CPR/92/120. For this service UNIDO-Vienna contracted Mr. A. D. Covington, consultant expert in tanning Chrome management and recovery.

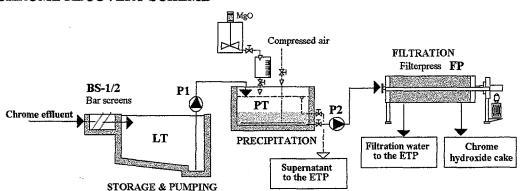
Because of the high fat content of the spent tanning liquor of the pig skins, the recovery is limited to the tanning liquors of the goat skin processing.

The adopted process consists of the following steps:

- a. Coarse filtration and storage of the spent tanning liquors.
- b. Chrome hydroxide precipitation with MgO.
- c. Hydroxide filtration by recessed plate filterpress.

The Cr-hydroxide cake is collected in sacks and consigned to the external factory for reprocessing.

#### CHROME RECOVERY SCHEME



#### 3.2.2 EFFLUENT TREATMENT PLANT

The here described plant is not exactly the "original" ETP, in fact two previous rehabilitation interventions had been planned and implemented in 1996 under the Project US/CPR/92/120:

- installation of a new mechanical sludge dewatering unit,
- construction of a second parallel clarifier for the sedimentation of the biological sludges.

These interventions had been designed by Prof. Haotin Wu, Vice Professor of Southeast University - Institute of Environmental Engineering of Nanjing, and Mr. M. Bosnic, UNIDO expert for tannery effluents.

The equipment for the sludge dewatering has been imported trough UNIDO-Vienna.

The sludge scraping mechanism of the new secondary sedimentation tank has been made locally.

# Brief description of the original ETP (see flow diagram No. 1)

The other tannery effluents, and the filtration waters of the Chrome hydroxide from the Chrome recovery plant, are collected in one main channel and sent by gravity to the ETP.

The mixed effluent after a coarse degreasing (gravity grease trap GT) and filtration (two manual bar screens BS1 and BS2 in series) is piped into two parallel pre-sedimentation tanks (PST-a/b) where the major part of the sand, lime and other heavy solids settle. The supernatant flows to the equalisation tank (ET) and the solids deposit is periodically removed by pumping (mobile vertical centrifugal pump P1).

The equalisation should be more properly defined "buffer" tank, in fact neither mixing nor aeration are implemented.

Three vertical centrifugal pumps (P2-a/b/c, two in operation and one stand-by) re-pump the effluent to the DAF units.

Three parallel flotation units (DAF-a/b/c) are installed (two in operation and one stand-by). No dosage of chemicals is performed.

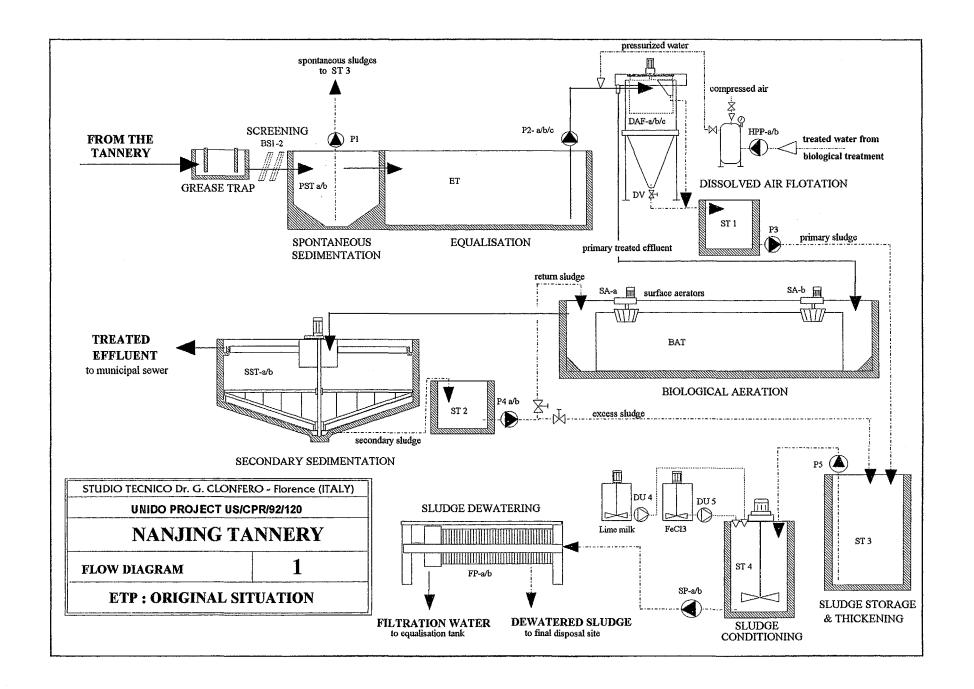
The DAF process is performed recycling and pressurising (horizontal centrifugal pumps HPP-a/b) part of the final effluent from the biological treatment.

The surface floated solids are constantly collected by a mechanical skimmer and discharged into the sludge tank (ST1). Possible settled materials are also periodically discharged in ST1 opening the manual drainage valves (DV) installed at the bottom of the DAF units.

The effluent from the DAF treatment is sent by gravity into the aeration tank (AT) of the biological process. The aerobic process is a completely mixed plug flow system performed in a ditch type "carousal", mixed and aerated by two surface aerators (SA-a/b).

The mixed liquor flows by gravity into two parallel secondary sedimentation tanks (SST-a/b) where the settled sludge is recycled (horizontal pumps P4-a/b) to the aeration tank and the supernatant discharged into the municipal sewer.

The excess of biological sludge is periodically by-passed to the sludge storage tank ST3.



All the produced sludges (spontaneous from PST, primary from DAF and surplus from biological treatment) are mixed in the storage & thickening tank ST3. Being ST3 not mechanised, some gravity thickening is obtained taking off manually the supernatant water that is re-pumped to the equalisation tank. The process is performed in batch and the sludge transfer pump (P5) is used for this purpose, taking off the superficial water layer with the flexible suction pipe.

The thickened sludge is then transferred (pump P5) to the sludge conditioning tank (ST4) where lime milk (DU4) and Iron chloride (DU5) is dosed. The chemical conditioning is performed in batch and the dosage of the chemicals is calculated on the transferred sludge volume. The sludge is mixed (vertical mixer MX) until complete reaction, and the dewatering process starts.

Two parallel dewatering units, consisting of high pressure membrane pumps (SP-a/b) and recessed plate filterpresses (FP-a/b), are installed.

The filtration waters are piped back to the equalisation tank.

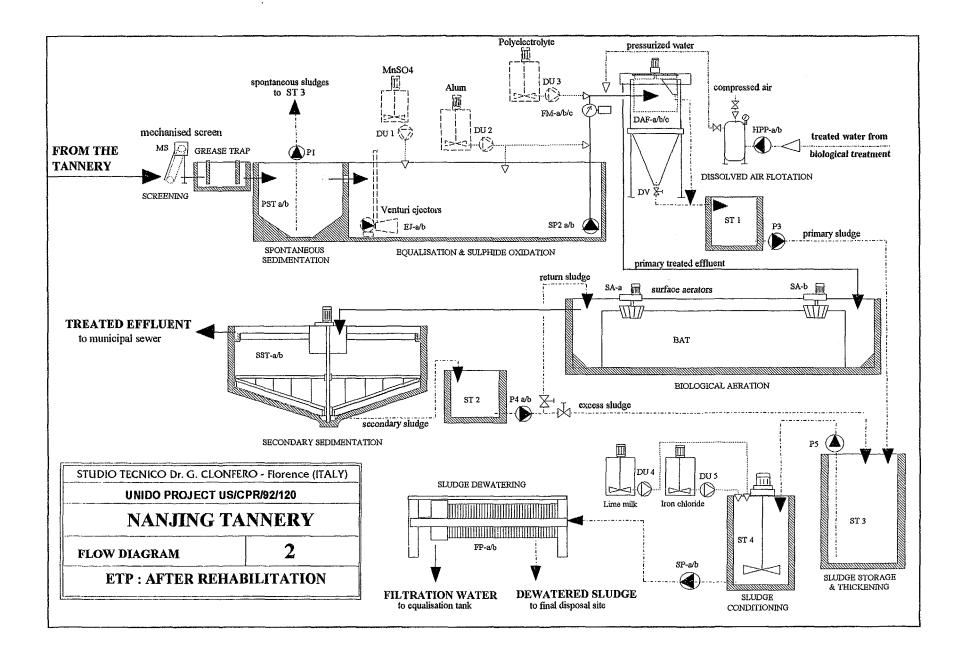
At the end of each filtration cycle, the dewatered cake is discharged (belt conveyor) in an adjacent area where is temporarily pile-stocked.

Periodically, the dewatered sludge (30-35% of DS), together with other solid wastes of the tannery, is collected by the lorries of the municipality service and transported to the final dumping site.

### Detected problems (p) and taken ameliorating interventions (i)

- p Poor efficiency of the bar screens. Many coarse solids (hairs, fleshings, etc.) settle in the spontaneous sedimentation tanks and in the equalisation tank. The quantity of these materials causes frequent clogging of the desludging pumps and their massive presence in the sludge risks to damage the filter press plates because of the obstruction of the internal feeding holes.
- i The installation of medium/fine mechanised screen (local) for a more reliable and efficient removal of hairs and other solid particles.
- p Insufficient volume and lack of a mixing/aeration systems of the equalisation tank.
- i Different technical alternatives have been proposed by Studio Tecnico and Mr. M. Bosnic, UNIDO consultant (refer to previous reports), but no provision has been taken until now (\*).
  - (\*) The past financial problems that forced the factory to stop the production are the reason of this delay.
- p Poor conditions and high maintenance of the locally made vertical pumps feeding the DAF units
- i Three new sets of submersible pumps (imported) for the feeding of DAF units have been provide through the project.

- p Poor efficiency and high maintenance problems of the locally made high pressure pumps for the recycle of the pressurised water to the DAF units.
- i Two new sets of high pressure horizontal centrifugal pumps (imported) for the recirculation of the pressurised water have been provide through the project.
- p Poor maintenance and improper operation of DAF units.
- i Correct operation information and training have been provided by Studio Tecnico (see Operation Manual and other relevant documents). Maintenance interventions (painting of steel structures, substitutions of corroded parts, etc.) must be performed by the factory's management.
- p Lack of apparatuses for both effluent analysis and in-plant monitoring. Neither portable nor on-line instrumentation for the operation/control of the ETP available.
- i The following apparatuses have been provided through the project:
  - three on-line flow-meters (instantaneous flow display and totalizer) for the correct operation & control of the flotation process,
  - one portable pH-meter for laboratory and on field measurements,
  - one portable DO-meter for laboratory and on field measurements,
  - one analytical balance, accuracy :  $\pm$  0.1 mg of 100 g capacity.



#### 3.3 DA CHANG COMPLEX (SHANGHAI RICHINA LEATHER Co.)

The Da Chang industrial complex consists of 3 tanneries. Presently only two tanneries are in operation, one for bovine hides producing wet-blue and finished upper leather (chrome tanning), and one for goat skin processing finished semi-aniline and corrected pigment for the local market.

The effluent of the two tanneries is treated in a common effluent treatment plant (CETP) and discharged into the municipal sewer.

Standards for discharge (see table).

**REMARK**: Shanghai regional environment authority adopted a regulation for the discharge in public sewer stricter than the national one.

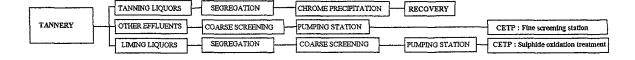
Parameter	National standards	Shanghai regional standards		
pН	6 - 9	6-9		
Colour	N.R.	50		
COD	500	100		
BOD <sub>5</sub>	300	60		
S2-	2.0	1.0		
N-NH3	N.R.	15		
tot. Cr	1.5	0.5		
Phenols	2.0	0.5		
O&G	100	20		
SS	400	60		

Shanghai standards for discharge into sewer

All parameters, except pH and colour, max. value in mg/L . N.R. means not required.

#### 3.3.1 PRE-TREATMENT AT THE FACTORY SITE

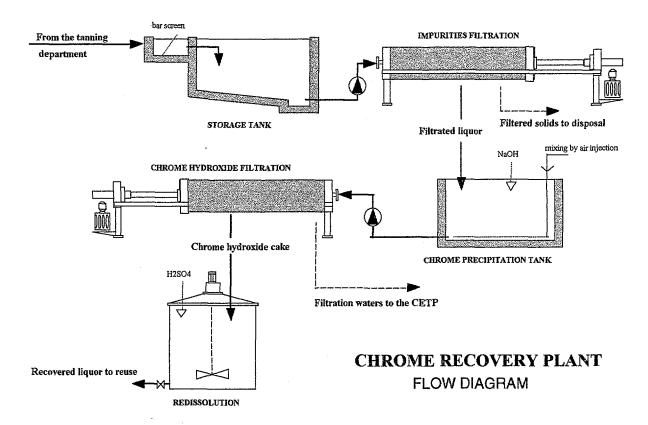
According with the original design 3 separate discharge lines and 3 pre-treatment units had been implemented at the factory site:



# **3.3.1.1 CHROME RECOVERY** (by precipitation, mechanical dewatering, redissolution and reuse).

The Chrome recovery process is the following (see flow diagram):

segregation of the Chrome liquors  $\Rightarrow$  coarse screening  $\Rightarrow$  storage  $\Rightarrow$  filtration of impurities by filter press  $\Rightarrow$  Chrome precipitation with Sodium hydroxide  $\Rightarrow$  filtration of the Chrome hydroxide by filter press  $\Rightarrow$  re-dissolution of the Chrome hydroxide with Sulphuric acid  $\Rightarrow$  reuse.



#### Detected problems (p) and taken ameliorating interventions (i)

- p Fluctuations in the Chrome concentration of the residual sludge generated by the CETP sometimes overcoming the national standard for use in agriculture (the Chinese norm GB 4284-84 "Control standards for pollutants in sludge for agricultural use" admits a max. content of 1,000 mg of Cr III per kg of dry sludge).
- i Studio Tecnico has recommended a more accurate segregation of the Chrome effluent, and a more appropriate operation of the recovery unit (see Chrome Recovery Manual), indicating proper operation and routine control procedures.

- p The present pre-treatment at Da Chang is limited to the chrome hydroxide precipitation and filtration, the chrome hydroxide cake is sold/dismissed to an external factory for reprocessing. The economical return, only 3-4% of the equivalent price of the commercial chrome sulphate salt, does not cover even the mere operation cost of the Chrome recovery treatment.
- i Studio Tecnico and other international UNIDO consultants have recommended the complete use of the Chrome recovery system, illustrating the positive experiences and results in other countries. The Da Chang tannery technicians started pilot-scale trials of recovered Chrome reuse.

#### 3.3.2 COMMON EFFLUENT TREATMENT PLANT

The original CETP was implemented in 1991 and was designed for the treatment of 10000 m<sup>3</sup>/day of effluents.

The tannery effluents enter the CETP by two separate pipelines: concentrated sulphide liquors and general effluent.

#### Pre-treatment of concentrated sulphide effluents

The sulphide liquors is carried out in batch. The are collected into 4 separate tanks (SOT-a/b/c/d). The tanks work in succession: when a tank is full, the new entering effluent is transferred in the adjacent empty tank.

The sulphide oxidation process is performed by aeration (low speed surface aerators SA-a/b/c/d) in presence of catalyst (MnSO<sub>4</sub>).

Ultimate the oxidation the liquor is transferred (pump P1-a/b) to the general effluent treatment (fine screening station).

#### General effluent treatment

The effluent from the factories and the pre-treated liming liquors are filtered through 4 rotary drum screens (RDS-a/b/c/d) working in parallel.

The filtered effluent, jointed in one channel, flows by gravity into the grit chamber (GC) and successively to the equalisation aeration tank.

The material from the grit chambers is periodically discharged and transported to the disposal site as a slurry.

Two parallel equalisation tanks (ET-a/b) are installed, each tank is subdivided into two parallel sections. The tanks are mixed/aerated by injection of air by blowers (ABL1-a/b) and submerged perforated pipes.

The mixed effluent is re-pumped (pumps P2-a/b/c/d/e) to the primary sedimentation tanks (PST-a/b). Two parallel sedimentation tanks are installed.

No chemical flocculation is performed.

The primary settled effluent enter by gravity the aeration tanks (AT-a/b) of the biological treatment. Each aeration tank is subdivided into 4 parallel sections. The aeration/mixing is realised by three blowers (ABL2-a/b/c). A fourth blower is the stand-by unit for both biological aeration and equalisation.

The mixed liquor from the aeration tanks flows by gravity into 4 parallel secondary sedimentation tanks (SST-a/b/c/d).

The sedimentation tanks have a mechanical scraping mechanism (SSM-a/b) for the collection of the settled sludge.

A series of Archimede screw pumps (ASP-a/b/c/d/e/f/g/h) continuously return the settled sludge to the aeration tanks.

The supernatant from the secondary sedimentation tanks flows by gravity into the tertiary treatment.

The tertiary treatment consists of a flocculation with Poly-Aluminium Chloride (PAC), followed by final sedimentation. Two parallel non-mechanised clarifiers (TST-a/b) with lamella plate media are installed.

Before the final discharge into the municipal sewer, the treated effluent may receive a final chlorination treatment. Two parallel chlorination chambers (CHC-a/b) are installed (\*).

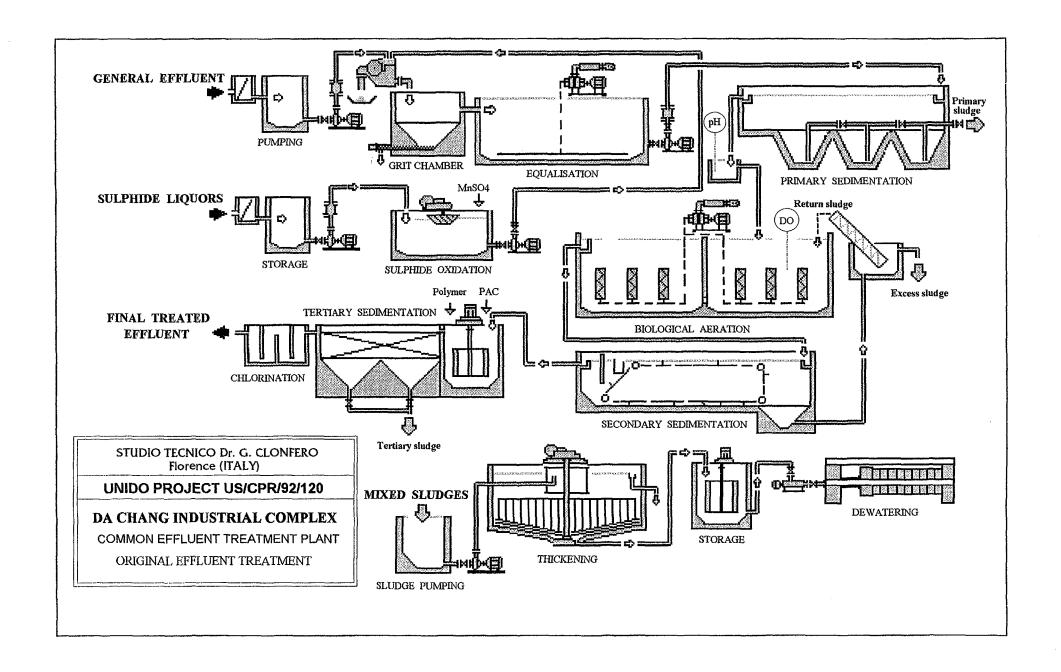
(\*) Note: the final chlorination had been never used because of the doubtful utility of such a process applied to effluents discharged into sewer. Furthermore the original design foresees the use of very hazardous chlorine in gaseous form.

#### Sludge treatment

The sludge from the primary sedimentation tanks, the surplus sludge from the biological treatment and the chemical sludge from tertiary sedimentation are jointed together (the discharge is by gravity) in a common sludge pumping station (SPS) and re-pumped (centrifugal pumps SP-a/b/c) to the sludge thickening process. Two parallel circular thickening tanks are installed (STT-a/b).

The supernatant water flows back to the effluent treatment, and thickened sludge is transferred by gravity in the sludge conditioning tanks (SCT-a/b/c/d). The four tanks work in parallel, and the process is carried out in batch. At the present, only PAC is used as conditioning chemical. The conditioned the sludge is finally mechanically dewatered by two recessed plate filter presses (FP-a/b).

The filtration water is piped back to the CETP.



#### Detected problems (p) and taken ameliorating interventions (i)

- p High and labour intensive maintenance of the sulphide oxidation department because of the quantity of hair and solids particles entering the unit.
- i One fine rotary-drum screen, complete of screw-press for the transport and squeezing of the filtered solids and automatic washing system, to be installed at the inlet of the sulphide oxidation treatment have been provide through the project.
- p Poor reliability and efficiency of the original non mechanised primary sedimentation tanks, and difficulty in desludging the non-mechanised primary sedimentation tanks.
- i The factory management has realised the necessary modifications of the civil works of one primary sedimentation tank, and the project has provided the travelling-bridge (imported) for sludge collection and removal.
- p Difficult evacuation of the primary sludge by gravity, causing periodic blockages of the pipes, deposits and bad small emission.
- i Two horizontal centrifugal pumps (1 + 1 stand-by unit) for the sludge transfer have been provided through the project.
- p Insufficient capacity and poor performance of the pumps for dosage of chemical(s) in the tertiary flocculation process.
- i Three new sets of dosing pumps (2 + 1 stand-by unit) of 0-1000 L/h capacity have been provided through the project for the tertiary flocculation treatment.
- p Insufficient capacity and low performance of the sludge dewatering department.
- i The poor performance of the sludge dewatering department was mainly related to the ineffective sludge handling system and conditioning method, therefore Studio Tecnico concentrated a relevant part of the in-plant training to the issue. Through a different sludge conditioning process (using FeCl<sub>3</sub>) and a more appropriate surveillance of the entire sludge treatment process, the capacity and performances of the sludge dewatering unit has been improved to a satisfactory acceptable level.
- p Poor maintenance of the imported equipment because of the lack of spare parts and standby units.
- i The project has provided the necessary spare parts and stand-by unit for the imported equipment:
  - spare parts for the scraping devices of the secondary sedimentation tank,
  - two new sets of filtering clothes for the filterpresses,
  - two new sets of helicoidal pumps feeding the filterpresses, and new spare parts.
  - two mobile submersible pumps for general maintenance and cleaning.

- p Lack of in-plant monitoring apparatuses.
- i The project has provided the following instrumentation:
  - two on-line pH-meters for monitoring of pH of the effluent coming from the equalisation tank,
  - two on-line DO-meters for the measurement of the oxygen levels in the biological aeration tanks,
  - one two-parameters recorder for continuous registration of pH and DO values,
  - one portable pH-meter for laboratory and on field measurements,
  - one portable DO-meter for laboratory and on field measurements,
  - four portable water samplers for the simultaneous collection of composite samples in different points of the CETP.
- p Difficulties in complying with the Shanghai regional standards for the Ammonia Nitrogen parameter: the original CETP was not designed for treating this pollutant (the regional discharge limit of 15 mg/L had been imposed successively).
- i Studio Tecnico has concentrated a relevant part of theoretical and on-spot training also to the issue (see Progress Reports of November 1998 and June 1999). Through the proper tuning of the biological treatment, and the pre-treatment of the most relevant N-NH<sub>3</sub> containing streams of the tannery, the concentration of the pollutant in the final effluent from 100 (max. 200) mg/L has been reduced to 40 (min. 10) mg/L. The experimentation is still in course, and a further improvement to reach the discharge limit is expected.
- p Absence of land fills for industrial solid wastes or other safe disposal alternatives for the dewatered sludge of the CETP.
- i The issue is specifically faced through the project US/CPR/97/022.
  - The definition of the optimum method for the final disposal/reuse of the sludge is not a simply technical but mainly an economical and legislative problem.
  - At the max, tannery production approx, 16-17 tons per day of dewatered sludge are expected, that, as a rule, should be daily transported to the final disposal site.
  - Presently the tannery confers the dewatered sludge to the solid wastes collection service of the municipality. The cost is not expensive, 50 60 RMB (6-7 US \$) per ton of waste, but nobody knows the possible future developments of the local situation.
  - In the Shanghai region there are no properly engineered landfills, neither for industrial nor for urban wastes, and the current disposal methods mostly consist in a uncontrolled spreading and abandoning of these residues onto the soil.

The tannery management is aware that this disposal way is very precarious and in any moment may be stopped by the local environmental authority.

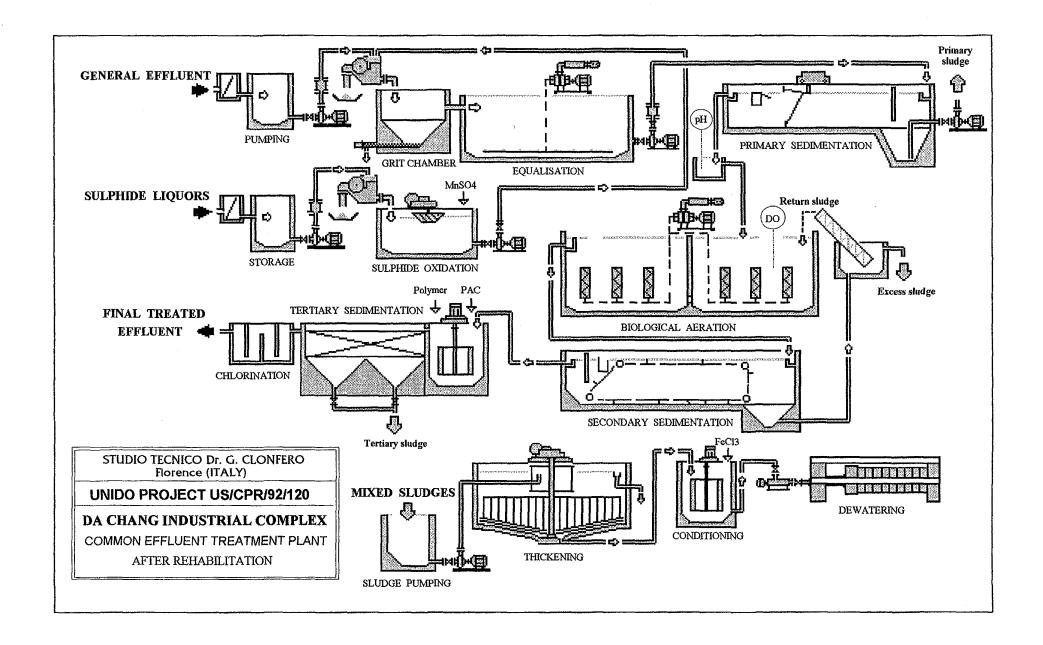
In 1995 the Chinese Government prepared a national legislation for solid wastes that contains general statements and basic principles, but does not establish neither technical criteria to be adopted nor standards to be respected. Therefore, a specific normative for the disposal of solid wastes and sludge does not exist in China.

Studio Tecnico considered the possibility that Shanghai Richina Co. will implement a private landfill, but the solution presents practical difficulties:

- the scarcity of land resources in the Shanghai region,
- the long bureaucratic procedures for leasing the land,
- the expensive price of the limited areas available,
- the geological characteristics of the region, with an abundant and very superficial water table, that do not allow deep soil digging, and therefore increase the implementation cost of the landfill.

Furthermore the present lack of technical norms and parameters does not facilitate the decision of the factory that cannot define any strategy of intervention and the necessary investment.

Considering all these difficulties and the uncertainty of the normative, Studio Tecnico has also explored (see Second Progress Report of June 1996) the possibility of implementing a temporary disposal area at factory site (stockpile), solution successively rejected by the factory' management for both economical and practical reasons.



#### 4. LEGISLATION SURVEY

#### CHINESE DISCHARGE STANDARDS (Norm GB 8978-88)

The Chinese Norm GB 8978-88 (Integrated Wastewater Discharge Standard) adopted in January 1989 contains:

- 1. classification of the receiving bodies in 3 groups or grades:
- Grade I: special protected areas,
- Grade II: developing and industrial areas, and sea,
- Grade III: sewer.
- 2. differentiation between new or expanded factories, and existing factories.
- 3. classification of pollutants in two main groups:
- group 1: Hg and Hg-organic complexes, Cd, and total Chrome, Cr VI, As, Pb, Ni, and Benzene derivates (*limits for group I are the same for any type of discharge*).
- group 2: all other pollutants.
- 4. maximum water consumption for the different industrial activities.
- 5. general discharge standards for all industries.
- 6. specific limitations for particular industries (the other parameters remain those of the general standards).

### Maximum admissible water consumption for leather processing

## Maximum permitted water consumption (m3/t)

(from Chinese Regulation GB 8978-88)

Processed material (raw material form)	Water consumption (litres/kg of raw material)			
	New or expanded factory	Existing factory		
Pig skins (wet salted)	60	70		
Bovine hides (dry)	100	120		
Goat skins (dry)	150	170		

#### **GENERAL STANDARDS**

Parameter (*)	Unit	Environmental Quality Standards				
		GRA	DE I	GRA	DE II	GRADE III
		A	В	A	В	A & B
pН	-	6-9	6-9	6-9	6-9	6-9
Colour	-	50	80	80	100	NA
SS	mg/L	70	100	200	250	400
BOD	mg/L	30	60	60	80	300
COD	mg/L	100	150	150	200	500
N-NH <sub>3</sub>	mg/L	15	25	25	40	NA
Phenols	mg/L	0.5	1.0	0.5	1.0	2.0
S2-	mg/L	1.0	1.0	1.0	2.0	2.0
tot. Cr	mg/L	1.5	1.5	1.5	1.5	1.5
O&G	mg/L	20	30	20	40	100

Notes:

Grade I special protected areas (drinking water, fishing or recreation)

Grade II industrial areas, developing areas, port or sea

Grade III sewer

A new or expanded factory.

B existing factory (in the year 1988).

(\*) only the parameters significant for tannery effluents have been considered.

NA not applicable

### SPECIFIC STANDARDS FOR LEATHER INDUSTRY

(new implemented or expanded tanneries)

		Chinese S	Standards	Expected characteristics of treated tannery effluent		
Parameter	Unit	Surface Municipal water sewer Grade II		Primary treatment	Primary & secondary treatment	
pН		6-9	6-9	6 -9	6.5 - 7.5	
Colour		80	NA	50 - 100	50 - 60	
N-NH <sub>3</sub>	mg/L	1	NA	100 - 150	10 - 15 (*)	
COD	mg/L	100	300	1000 -1500	150 - 200	
BOD	mg/L	30	150	500 - 1000	20 - 30	
Sulphide	mg/L	1	2	1 - 2	0 - traces	
Phenols	mg/L	0.5	2	(**)	0 - traces	
O&G	mg/L	20	100	50 - 100	10 - 20	
tot. Cr	mg/L	1.5	1.5	1 - 2	0 - traces	
SS	mg/L	80	200	50 - 100	50 - 80	

(\*) (\*\*) for biological treatment including BOD removal and <u>nitrification</u>. very variable (it depends from processing method and used chemicals)

NA not applicable

## **ANNEXES**

## ANNEX 1: REPORTS AND MANUALS - Contract 95/230 P

Year	Date	Report/Document	Title
1996			
	March	FLASH PROGRESS REPORT	All Project Sites: Encountered Situation and First Mission Findings
	June	FIRST PROGRESS REPORT (Part A)	Xian Tannery: Rehabilitation Design of the ETP
	11	FIRST PROGRESS REPORT (Part B)	Nanjing Tannery: Rehabilitation Design of the ETP at
	September	SECOND PROGRESS REPORT (Part A)	Da Chang Ind. Complex: Feasibility Study of a Landfill for Tannery Sludges
	!!	SECOND PROGRESS REPORT (Part B)	Da Chang Ind. Complex: Feasibility Study and Adaptation of an Area for the
			Temporary Disposal/Storage of De-watered Tannery Sludges
1997	May	BASIC MANUAL	Da Chang Ind. Complex: Rehabilitation of the CETP
!	31	BASIC MANUAL	Xian Tannery: Rehabilitation of the ETP
	11	BASIC MANUAL	Nanjing Tannery: Rehabilitation of the ETP
	September	THIRD MISSION REPORT	Da Chang Ind. Complex: CETP Situation and Performed Activity
1998	January	FOURTH MISSION REPORT	All Project Sites: General Situation, Progresses and Existing Problems, On-
			site Training.
	April	OPERATION MANUAL	Da Chang Ind. Complex: Rehabilitation of the CETP
	May	OPERATION MANUAL	Xian Tannery: Rehabilitation of the ETP
	"	OPERATION MANUAL	Nanjing Tannery: Rehabilitation of the ETP
	"	BASIC & OPERATION MANUAL	Da Chang Ind. Complex: Chrome Pretreatment and Recovery
	11	BASIC & OPERATION MANUAL	Xian Tannery: Rehabilitation of the Chrome Recovery Plant
	11	BASIC & OPERATION MANUAL	Nanjing Tannery: Chrome Treatment and Recovery
	November	TECHNICAL LECTURE	The 4th Asian International Conference of the Leather Science & Technology,
			Beijing: The S. Croce Leather District
	11	TECHNICAL LECTURE	The 4th Asian International Conference of the Leather Science & Technology,
			Beijing: Chrome pre-treatment & Recovery
1999	January	FIFTH PROGRESS REPORT	All Project Sites: Mission Report, General Situation and On-site Training
	11	NOTE FOR THE FILE	All Project Sites: Problems and Corrective Actions
	June	SIXTH PROGRESS REPORT	Da Chang Ind. Complex: Screen installation and Ammonia removal, On-site
			Training

## ANNEX 2: MISSION TO THE PROJECT SITES - Contract 95/230 P

	Period	Project sites	Expert	Functions	Duration m/m	Total m/m	Main activity	
1996	13-28 Jan.	Shanghai, Nanjing	Clonfero	Team Leader	0.5	0.5	Preliminary on-site inspection & data collection.	
	10-24 Mar	Beijing, Nanjing, Xian, Shanghai	Clonfero	Team Leader	0.5	1.0	Data consolidation and work programme.	
	23 Apr07 May	HK, Nanjing, Shanghai	Clonfero	Team Leader & Expert in Tannery Effluent Treatment	0.5	1.5	Meeting with CLIA, illustration of ETP rehabilitation interventions, equipment definition.	
	27 Apr07 May	Shanghai	Bruni	Senior Geologist	0.3	1.8	Sludge treatment & disposal. Site inspection, Short Course on Safe Sludge Disposal Methods, Meeting with Local Authorities.	
	27 Apr07 May	Shanghai	Del Monaco	Senior Engineer Expert in Tannery Sludge Disposal and Landfill Design and Operation	0.3	2.1	Sludge treatment & disposal. Site inspection, Short Course on Safe Sludge Disposal Methods, Meeting with Local Authorities.	
	02-28 Sept.	Shanghai	Clonfero	Expert in Tannery Effluent Treatment & Plant Monitory	0.9	3.0	Equipment Installation & On-site Training, Effluent Laboratory Procedures.	
1997	7 18 Jan09 Feb. Shanghai, Xian, Clonfero Expert in Tannery Effluent Xu-Zhou, Beijing Treatment & Plant Monitory		0.7	3.7	On-site Training (continuation), Project Dissemination.			
	12-28 Jul.	12-28 Jul. Shanghai Clonfero Expert in ETP Operation & Laboratory Procedures		0.5	4.2	On-site training (continuation) in CETP Operation & Monitoring,		
	29 Nov 18 Dec.	Shanghai, Xian	Clonfero	Senior Engineer Expert in Tannery ETP Design, Implementation and Monitoring	0.6	4.8	On-site training, equipment installation, Chrome Recovery & Reuse.	
1998	19 Aug06, Sept.	Shanghai, Nanjing, Xian, Beijing	Clonfero	Senior Environmental Engineer Expert in Plant Operation & Monitoring	0.7	5,5	New Equipment Installation, On-site Training, Meeting with CLIA.	
	21-27 Nov.	Beijing	Clonfero	Team Leader & Tannery Effluent Expert	0.2	5.7	Lectures and meeting with UNIDO and CLIA.	
1999	23 Apr 01 may	Shanghai	Clonfero	Team Leader & Tannery Effluent Expert	0,3	6.0	On-spot training: Ammonia removal, tuning of the biological process, and other issues	

## ANNEX 3: MEETINGS AT UNIDO HEADQUARTERS - Contract 95/230 P

	Period	UNIDO	Expert	Duration	Main activity
				days	
1996	07 Feb.	Vienna Headquarters	Team Leader	1	Briefing
	28-29 Mar	Vienna Headquarters	Team Leader	2	Interim briefing/consultation
	12-13 Dec.	Vienna Headquarters	Team Leader	2	Selection of equipment for Xian and Nanjing ETPs
	16 Dec.	Vienna Headquarters	Team Leader	1	Selection of equipment for Xian and Nanjing ETPs
1997	20-23 May	Madras RPO	Team Leader	4	Interim briefing/consultation, performed activity & findings
1998	26 May	Vienna Headquarters	Team Leader	1	Performed activities and findings