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UNIDO
**Regional Programme for Pollution Control in the
Tanning Industry in South East Asia**

US/RAS/92/120
Contract n°97/049-Amendment B

May 2001

**Final report of the mission of Michel ALOY
in Chennai - India
from 20th February 2000 to 8th February 2001**

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Abbreviations

BCS	Basic Chromium Sulphate
BOD ₅	Biochemical Oxygen Demand, 5 days at 20°C
BOD ₂₀	Biochemical Oxygen Demand, 20 days at 20°C
°C	degree Celsius
CETP	Common Effluent Treatment Plant
CLRI	Central Leather Research Institute in Chennai, Tamil Nadu, India
cm	centimetre
COD	Chemical Oxygen Demand
CTC	Centre Technique Cuir Chaussure Maroquinerie, Lyon, France
d	day
DO	Dissolved Oxygen
DS	Dry Solids
EC	Electrical Conductivity
EI	East Indian (vegetable tanned leather)
ETP	Effluent Treatment Plant
ft	foot (30.5 cm)
g	gram
h	hour
ha	hectare (10,000 m ²)
HVLP	High Volume Low Pressure (spray guns)
IST	Intermediate Storage Tank
IULTCS	International Union of Leather Technicians and Chemists Societies
kg	kilogram
kg/cm ²	kg per square centimetre
kW	kilowatt
kWh	kilowatt hour
l	litre
M	molar
m	meter
m ²	square meter
m ³	cubic meter
mg/l	milligramme per litre
MgO	Magnesium oxide
ml	millilitre
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
mmhos/cm	millimhos per centimeter
mn	minute
m/s	meter per second
N	normal
Na ₂ S	Sodium sulphide
PDU	Project Demonstration Unit
pH	negative logarithm of hydrogen ion concentration
ppm	parts per million
RCC	Reinforced cement concrete
RePO	UNIDO Regional Programme Office in Chennai, India

RO	Reverse Osmosis
Rs	Rupees (Indian)
rpm	round per minute
s	second
SS	Stainless steel
t	tonne (1000 kg)
TDS	Total Dissolved Solids
TNPCB	Tamil Nadu Pollution Control Board
TS	Total Solids
TSS	Total Suspended Solids
UASB	Up-flow Anaerobic Sludge Blanket
UNIDO	United Nations Industrial Development Organisation
UV	Ultra Violet
VS	Volatile Solids
W	watts

1. Introduction

This mission was organised within the contract 97/049 - Amendment B, following the main part of the project US/RAS/92/120 (Contract 97/049) between May 1997 and May 1999, and the Contract 97/049 - Amendment A, from May 1999 to January 2000.

This mission was divided in homework and three distinct visits in India, the first one from 20th to 26th February 2000, the second from 5th to 17th July 2000, and the last one from 28th January to 8th February 2001. Discussions and meetings took place at Regional Programme Office (RePO) and at Central Leather Research Institute (CLRI) in Chennai. Technical visits were organised in Ambur, Ranipet, Melvisharam, Kannivakkam and Vanyambadi. These visits in India were organised to control most of the operation been carried out with various PDU and other technical inputs.

Between these visits, technical support was provided from CTC France to review technical papers prepared by RePO.

During this contract, Michel Aloy from CTC was acting as the main source of expertise and technical adviser for applied research programmes organised by the UNIDO Office in Chennai, in cooperation with local tanners. He was mainly in contact with the Project Manager, Leather Unit, SES/AGR in Vienna and with the Programme Coordinator and other staff of the RePO IN Chennai, as well as with other international and national consultants, experts and national counterparts.

Detailed comments are recorded.

2. PDU Review

2.1. PDU/1 Reed beds

Presidency Kid Leather (Kannivakkam) reed beds

The reed beds are showing good conditions and the visual aspect of the reeds confirms the good selection of parallel feeding. The average latest results, taking into account the activity in the three beds are as follows:

Month	Flow Rate m ³ /d	BOD ₅ offer mg/l	COD offer mg/l	Elimination rate		Specific elimination g/m ² /d	
				BOD ₅	COD	BOD ₅	COD
AUG. 2000	55,81	696	1935	71,8%	46,5%	15,7	28,8
SEP. 2000	58,00	684	2035	76,6%	61,3%	16,3	39,2
OCT. 2000	53,76	497	1640	75,1%	57,6%	11,8	30,0
NOV. 2000	48,24	593	1900	82,6%	60,9%	13,8	32,7
DEC. 2000	49,83	615	1838	83,4%	59,1%	14,3	30,7

It can be seen that the results obtained are not so high than in Melvisharam. It is probably due to the low biodegradability of the effluent processed, as the COD/BOD₅ ratio is 3.03 for the five months in PKL and 2.6 for the results from August 1999 up to December 2000. For the last two months of 2000, where the results of Melvisharam are very good, the COD/BOD₅ ratio is 1.8 for November and 2.1 for December. These ratios are not very common for tannery effluent and they can be seen mostly with domestic sewage.

The ratios, in terms of pollution eliminated per square meter are not very high and the objective for the next month could be to increase the quantity of effluent to be sent in the reed beds. However as half of the effluent is coming from secondary treated effluent, it can be stated that the remaining COD is hardly degradable. If we take into account only the COD brought with primary effluent, that is to say 75 % of the total COD offer, the percentage of degradation is higher and it has reached 83 % of the COD in December, much more than the value of 59.1 %. So it would be highly interesting as BOD₅ of the secondary effluent is very low, to test the recycling of the outlet of reed beds by pumping and send one third of the flow in each bed, jointly with the primary treated effluent. The recycling rate of the reed beds could be around 50 %.

Melvisharam reed beds

The Melvisharam reed bed planted mostly with typha, is in good growing conditions. Reeds are green and the pollution elimination results are quite impressive, mainly for the last months. The last results are indicated in the following table:

Month	Flow Rate m ³ /d	BOD ₅ offer mg/l	COD offer mg/l	Elimination rate		Specific elimination g/m ² /d	
				BOD ₅	COD	BOD ₅	COD
AUG.1999	46,6	800	1808	46%	41%	12,2	24,5
SEP.1999	44,3	753	1729	87%	76%	20,5	41,4
OCT.1999	32,6	731	1667	93%	82%	15,7	31,7
NOV.1999	34,3	681	2044	94%	80%	15,6	39,5
DEC.1999	46,3	685	1866	91%	70%	20,4	42,8
JAN.2000	47,5	753	2186	92%	72%	23,3	52,6
FEB.2000	34,5	795	2014	90%	73%	17,4	35,6
MAR.2000	21,2	666	2270	88%	73%	8,8	24,9
SEP.2000	21,1	318	1275	89%	70%	9,6	32,9
OCT.2000	15,9	431	1278	84%	73%	9,3	24,5
NOV.2000	39,8	694	1253	92%	78%	41,0	64,4
DEC.2000	47,5	649	1347	93%	78%	45,1	81,6

The quantity of effluent to be delivered to this reed bed could be progressively increased up to 100 m³ per day.

A new proposal is being prepared to upgrade the existing reed bed in order to minimise the impact of suspended solids coming from the clarifloculator, improve the hydraulic distribution within the bed, improve the overall aspect of the reeds, modify the outlet scheme to recycle an important part of the effluent. All these elements are included in a proposal prepared by The Solution Centre from Cochín.

Ranipet experiment

The results of this small experimental reed bed used as a tertiary treatment are good, but not so high in quality when compared to the physico-chemical treatment. It is however interesting to note that phragmites have demonstrated a good ability to grow in such a saline effluent exceeding 10,000 mg/l in TDS and 5,000 in chloride. Although not showing the same development, trema and typha are also in good conditions. No further development is foreseen in Ranipet for the moment. Nevertheless, the performances for six months experiment (June to December 2000) have shown a removal rate of 40 % for COD giving a final value of 235 mg/l, and an elimination rate of 54 % for BOD₅ with a final value of 12 mg/l. These two values are within the limits of Tamil Nadu legislation.

Sidco experiment

The reed bed was issued from the conversion of sand filter (size: 11 m x 5 m x 1.15 m) into an experimental reed bed and regular feeding and monitoring were

done from 20 August 1998 onwards. Out of 22 m³ total capacity 4.4 m³ of effluent is withdrawn on batch wise basis every morning from the filled up bed and an equal quantity of treated effluent is fed from CETP to maintain about 5 days retention time.

Out of the two varieties planted, Typha survived and fresh shoots started coming but the Sachharum almost died completely. Salient analytical values are given hereafter:

Parameter	Unit	Influent to reed bed	Effluent from reed bed	Elimination %
		Average value	Average value	
pH		7.55	7.4	
TS	mg/l	4455	4420	1%
TDS	mg/l	4410	4420	0%
TSS	mg/l	155	45	71%
Chlorides	mg/l	810	810	0%
Sulphides	mg/l	BDL	BDL	
Sulphates	mg/l	1010	1005	0%
COD	mg/l	314	146	54%
D.O.	mg/l	2.3	2.4	-4%

The fill and draw system is operated in good condition with 5 days detention time, but no new development was discussed and no extension of the reed bed is foreseen. From April 99 to December 2000, the performances on secondary treated effluent are 40 % removal of COD (228 mg/l), 52 % for BOD₅ (13 mg/l) and 88 % for colour removal (85 Pt-Co units).

Conclusion

This technology is more adapted to small-scale tanneries and can replace with good results the biological treatment step. Energy savings and absence of permanent control are the main benefits of this technology. Although the investment is low, the area required by the treatment may sometimes be difficult to find for tanneries located inside a cluster.

This technology can hardly be considered as a very interesting option for tertiary treatment, except for colour removal of vegetable tannery effluent. This technology does not support the shock loads and is necessarily a second step of treatment after a primary physico-chemical treatment.

3.2. PDU/2A TDS Removal with Reverse Osmosis

Tannery effluent being processed through physico-chemical (primary) and biological (secondary) treatment are containing very high level of total dissolved solids TDS that cannot be removed through classical waste water treatment. Evaporation can be used, but with artificial heating the energy spent brings very high. Natural evaporation requires very large ground surface and evaporated water cannot be recovered. Membrane technologies, and mainly reverse osmosis RO, are adapted to separate TDS from water.

The objective of this PDU was to test RO technology with treated tannery effluent and to evaluate the achievable results, advantages and problems of the technology and costs of such a process.

A pilot plant was installed in a tannery having its own effluent treatment plant with a physico-chemical and a biological treatment. This pilot plant was designed to process 1 m³/h of secondary treated effluent. The processed effluent had the average analytical values:

Parameters	Average value	Range
pH	7.8	6.7-8.2
Total Suspended Solids mg/l	212	145-234
Total Dissolved Solids mg/l	5010	3040-6110
BOD ₅ mg/l	62	38-72
COD mg/l	412	175-510
Chlorides mg/l	1020	810-1840
Total hardness mg/l	1750	1400-1904

The pilot plant was installed by ACS Company. It consists of the following equipment

- a raw water collection tank of 1 m³
- a centrifugal closed impeller raw water pump of 0.75 kW (capacity 2 m³/h)
- an inlet water tank of 0.5 m³
- a centrifugal closed impeller raw water pump of 1.5 kW (capacity 3 m³/h)
- a multi-grade filter 100 l with garnet and anthracite media (capacity 4 m³/h)
- two photo-chemical oxidiser in series with UV lamps
- an activated carbon filter 100 l with granular activated carbon (capacity 4 m³/h)
- a softener 100 l with strong acid cation resin (capacity 6 m³/h)
- four chemical dosing units (100 l) with dosing pumps (1 l/h) for hydrochloric acid, antioxidant, antiscalant and hydrogen peroxide

- a cartridge filter of 28 l with 5 μ mesh for 3 m³/h
- two 500 l intermediate storage tanks
- a high pressure (15 kg/cm²) piston pump 2.25 kW (capacity 3 m³/h)
- two spiral wound nanofiltration units (10 Angstrom pore size) tubes for 15 l/m²/h
- a high pressure (35 kg/cm²) piston pump 4 kW (capacity 3 m³/h)
- two spiral wound reverse osmosis units (0.2 Angstrom pore size) tubes for 30 l/m²/h
- a permeate collection tank of 1000 l

For six months the pilot was operated during eight hours per day (one shift) and no major problem occurred except a failure in the sealing of the membrane in the tube, probably due to the hydrogen peroxide needed to oxidise organic residual matters. The addition of this chemical was deleted and after several months of operation, it was possible to establish a material balance giving around 75 % of recovered float with less than 400 mg/l of TDS.

With 24 hours operations, the material balance is lower and 70 % of the processed effluent can be recovered and used in tannery process, at dyeing stage, without any problem. With longer experiment clogging problems of the membrane are occurring and it is necessary to find new procedures to clean the membrane. The management of the rejects of the membrane and of the effluent of the regeneration effluent from the softener have to be taken into account as the material balance have shown their high incidence in the process.

After three months of 24 hours operations some clogging was observed on nanofiltration membrane. However, one part of responsibility can be given to malfunctioning of the ETP facing the animal of unfixed dye.

Site visit at ATH tannery

During this visit, it was possible to see the RO system in operation. Data are well recorded and it was possible to see the latest results obtained. The system is operated 8 hours per day and average value of TDS obtained in the permeate is around 500 mg/l (between 450 and 550 mg/l), starting from an effluent with 5000 mg/l. Pressure in RO1 is about 10 to 15 bars and in RO2 from 15 to 20 bars. When pressure increases, a cleaning of the membrane is done. This comes every 3 days (after 24 hours of operations). Regeneration of the softener is operated every day and lasts one hour. The permeate recovery rate is between 70 to 75 %. All control equipment is running in good conditions, including inlet and outlet electromagnetic flow meters.

These recovery rates were confirmed during a joined trial with ACS, CLRI and RePO, on 23-24 October 2000. The objectives of this test were:

- To measure the flow rates at various sections of the unit to prepare the water balance in the operation of the system
- To collect a final set of samples

- To observe the general operation conditions

The following conditions were confirmed:

- TDS inlet and outlet are respectively from 5000-5500 to 100-350 mg/l
- Total running time of the plant was 30 hours
- Backwashing of pressure filter and activated carbon filter was done two times during the trial period for 5 minutes each.
- The membrane flushing was done using around 200 litres each of permeate water, which has been retained in the IST-1 and IST-2 for further operations.
- The total inflow during the period was 22 m³.
- The total reject was 4.92 m³. The backwash water represented 832 litres.
- 200 litres were used for the cleaning of the membranes.
- The miscellaneous losses are estimated at around 0.5 m³.
- The total quantity of water rejected was 6.46 m³ and estimated permeate quantity was 15.55 m³, which indicates a recovery rate of 70.7%.

The following values have been set up for RO treatment :

Parameter	Unit	Quantity
Average quantity of water treated (20 h operation)	m ³ /day	220
Average quantity of water recovered (20 h operation)	m ³ /day	154
Cost of operation	US\$/day	137.2
Cost operation /quantity of water treated	US\$/m ³	0.62
Cost operation /quantity of water recovered	US\$/m ³	0.89

Compared to the purchase value of fresh water bought by tanners for dyeing purposes in south of India (around 0.72 US\$ per m³), it can be said that the cost of recovery is 24 % higher than the cost of fresh water. However, the water purchased has a TDS content of 1500 to 1750 mg/l instead of 300-400 mg/l for RO recovered water. Taking into account the purchase cost for good quality water, the real cost of treatment for TDS is only 0.89 – 0.72 = 0.17 US\$ per m³ of water recovered.

It is also necessary to take into account the reject volume from RO. However the salt quality of the reject is quite high and evaporation gives the possibility to recover some salt that could be used for hide and skins preservation.

Conclusion

The experiments, performed at industrial scale in an Indian tannery, have proven the technical feasibility of the RO process for TDS elimination. However several

problems occurring during the experiment have demonstrated that the membrane life can hardly exceed one year and half. Even in these conditions, the economical viability of the project is not far to be demonstrated taking into account the heavy impact of TDS in south of India. However, the main difficulty concerns the high volume of the reject that can hardly represent less than 25 % of the processed volume of tannery effluent. This percentage could be reduced if some cleaner technologies are applied such as the prevention of salt curing for skins, the direct recycling of pickling liquors or the selection of saltless chemicals in the tannery process when it is economically feasible.

A practical solution has to be established for the reject and evaporation (natural or accelerated) can give the possibility to recover some good quality salt, with some possibility of reuse for hide preservation.

An up scaling of the project, with a modified pre-treatment scheme, is recommended to evaluate the reliability and the running cost of such a process. Two proposals were prepared for 200 m³/d and 4000 m³/d. The main point to be taken into account is the organisation of the pre-treatment in order to reduce the use of chemicals, protect the membranes, and limit the rejected volumes.

3.3. PDU/3 Fleshings in UASB reactor

Tannery effluent can be processed through anaerobic treatment to reduce the oxidable matters. An experiment was carried out at CLRI to evaluate the operational parameters of such a process, including the recovery of methane produced through the process. Tannery fleshings can be processed through anaerobic treatment to produce gas, as major component from fleshings is organic matter.

By mixing the two components, effluent and fleshing, it could be possible to reduce the waste volume produced by the tanneries and to generate gas useful for electricity production needed for tannery equipment.

The objective of this PDU was to test the feasibility of the anaerobic process technology with tannery waste and to evaluate the technical parameters and costs of such a process.

A UASB pilot plant was already installed and available at CLRI in Chennai. This pilot plant was used to process tannery effluent coming from Pallavaram tanneries and the results obtained were quite satisfactory for this type of treatment.

In order to find the best adapted solutions to add fleshing to the system, some mechanical and chemical procedures were evaluated. Beside expensive mechanical equipment, it was found that using the treated effluent coming from the UASB reactor, it was possible to degrade within ten days at ambient temperature (30-40°C) the mechanical fleshing collected in Pallavaram tanneries.

Due to wide variations of humidity and organic part of fleshing, it has not been established any degradation figures in respect to the temperature and dilution ratio. However, the mixture 50/50 of fleshings in effluent from UASB reactor is quite suitable for degradation of the mechanical fleshings in South Indian weather conditions during ten days.

The addition of liquefied fleshings obtained was tested at increasing rates from 30 to 100 kg of raw fleshings per day (60 to 200 kg of liquefied slurry) with 15 m³ sent to UASB operated with a contact time of 20 hours. The observed increase in COD of the influent was about 10 % for 75 kg of fleshing added. However, the reduction of COD obtained during the UASB process does not vary in large proportion and remains around 65 % of the inlet. The biogas obtained in the UASB reactor was increased by 10-12 % proportionate to the increase of the COD load. No important variation in the UASB sludge quality was observed.

Some tests have been carried out to determine in which exact conditions is obtained the liquefaction of organic matter coming from wet fleshing (0.8 kg of wet fleshing) and 0.8 litres of effluent from UASB. After 17 days at 30°C, under mixing, soluble COD, is increased from 5,000 mg/l to 53,500 mg/l giving a solubilisation of 55-62 % of the fleshing (organic part).

However, some solid waste is transformed into liquid waste, with only 65 % elimination of the organic pollution (COD). This does not appear as the best solution for fleshings. Biomethane process, where fleshings are mixed with sludge, seems more profitable as volume processed is reduced by 30 to 50 %. Residual waste can be used for composting and energy recovery is at an interesting level (615 litres of gas per kg of volatile matter processed).

Conclusion

Although it is much more profitable to use fleshings for the production of animal foodstuff, in the light of the recent development in Europe, this should be at least restricted to foodstuff for carnivorous animals. However due to BSE disease transmission, it seems logical to seek for alternative recovery routes.

The use of fleshings in an anaerobic reactor is only adapted to sites where UASB exists and the available quantity of fleshings cannot justify any recovery to produce technical gelatine. The interest of such a process is limited as a UASB treatment of effluent is required. About 2.5 litres of gas per kg of COD destroyed are produced.

If these experiments have proven the feasibility of the process, the environmental aspect of fleshing liquefaction in regard of air pollution and bad smells was under estimated..

3.4. PDU/4 Biomethanation

Technical meeting at RePO

A technical meeting with Mr R.A. Ramanujam and Mr Shanmugham was held at RePO on 31st January and the last months' situation presented.

During the month of October, up to the 20th, the feeding was about 2.5 to 3 m³ per day of fleshings and sludge and the gas produced reached the level of 40 to 45 m³ per day. Due to the breaking of the cutter the feeding was stopped, but the gas production was still for some days about 30 to 40 m³ per day. In November, it was no more possible to collect any fleshing in the Melvisharam area and only primary sludge was used occasionally for the process. Then the gas decreased to 15 m³ per day, even lower some days. From 15 to 29 November no feeding was taking place.

On the 30th November a new feeding of 1.5 m³ of fleshing was sent to digesters. In December, with 3 to 3.5 m³ of mixture containing 1.5 m³ of fleshings, the gas production was between 25 to 32 m³ reaching 37 m³ per day at the end of the month. At the beginning of the year 2001, from 4th to 20th January, some cow dung was added at the rate of 1.5 m³ per day and the gas production increased up to 50 m³ per day. On the last week of January, when the gas production increased up to 65 m³ per day, the feed rate was about 3.5 to 4.5 m³ of mixture per day representing 175 to 200 kg of volatile solids. In the first week of February, on 3rd February the gas volume was 75 m³ and on 5th the gas volume reaches 82 m³.

As shown in the last results obtained, there is no possibility to increase the gas production if the following conditions are not fulfilled:

- A regular feeding, constant in quality and containing the required volatile solids. The bacteria used for the process, either acidifying or methanogenous are sensitive to load variations.
- A proper maintenance of the sensitive parts of the system such as the mincer knife and hole plate.

A lot of spare parts is now available for the mincer and the hole plates and knife can be manufactured now in India in a place close to Melvisharam.

The main objective of the following months will be to have a constant feeding to assess the real capacity of gas production with an ambient temperature around 30°C.

Checking the bacteria used for the process, it was established that in the French experiment, more than 90 % were acidifying bacteria and 10 % methanogenous and less than 1 % sulphate reducing bacteria.

When analysing the volatile fatty acids, an increase of the ratio of propionic acid over 20 % shows a degradation of the process.

Site visit on 1st February

During this site visit, it was possible to see large quantities of fleshings ready for grinding. Some corrosion is visible on the gas tank and it needs to be repainted. This will be done in a few days. One of the two centrifuge mixing pumps was out of service for repair. The liquid of the scrubbing system for the gas needs to be renewed and IISc must come to check and control the sulphide removal plant.

During the discussion with Mr Shanmugham from CLRI, the following points were stated:

- To increase the volatile solids in digesters, the outlet of digester 2 will be the overflow pipe, directly connected to the digester drain chamber. When the digester 1 will be filled, automatically the digester 2 will release the equivalent volume from the upper part.
- The feeding of the system should be as regular as possible in term of quality and quantity.

- The addition of cow dung can be used only to accelerate the restarting of the digester following an accident. There is no reason to add such seed during the normal running of the system.
- Clogging problems occurring in the feeding pipe coming from the mixing tank are probably the result from long periods without any feeding. Before any pipe modification, it should be better to clean regularly the pipe with pressure system. If some pipe modification is needed, it is necessary to test if the increase of the size of the pipe should not reduce too much the velocity of the mixture and thus increasing the deposit.
- At the latest stage of the experiment, when the normal feeding will be obtained on a regular basis (ambient temperature and 5 tonnes per day or 585 kg of VS), if the gas production cannot be considered as satisfying, an increase of temperature of the mixture could be tested up to 35°C. For example, it could be possible to place a heat exchanger with a gas boiler on one of the mixing circuit of digester 1. Normally the gas consumption should not exceed 10 % of the gas production.

All these points were confirmed during a meeting with Mr R.A. Ramanujam and Solomon Sanpathkumar at RePO office on 6th February 2001.

Reasonably the gas production could reach 200 m³ given the lower level of volatile solids and the lower dry solids content in the fleshings, as well as the higher inorganic solids in sludge. The increase of the gas production over this value implies a better quality of fleshings and more volatile solids in the sludge.

Conclusion

Despite mechanical failures and lack of control of the material introduced inside the digesters, biomethanation is a valuable solution when no recovery option exists for fleshings. Given the indications observed during the experiment in India, some simplifications can be evaluated for a larger plant, to improve the reliability and to limit mixing cycles in the digesters. Construction materials of the digesters needs to be corrosion proof and concrete is a better solution for large size digesters. The weak part of the system remains the necessity to obtain finely divided fleshing material. However, with a different introduction system into the digesters, such as an existing piston pump adapted for fleshings, and a gas mixing instead of the hydraulic mixing, it could be possible to delete the mincing system and to operate the biomethanation process with more reliability.

Given the characteristics of the infeed, a new material balance was prepared by RePO and a gas production of 188 m³/day to be obtained from 4 tons of fleshings (15 % Dry Solids and 55 % Volatile Solids) and from 1 ton primary sludge (5 % DS and 35 % VS).

3.5. PDU/5 Mechanical and chemical treatment of fleshings

Fleshings obtained during leather processing are a source of protein and grease that are the main constituents of the dry part of this tannery waste. Some plants

have been established in developed countries to separate water from grease and proteins and recover grease for industrial purposes and protein for animal foodstuff.

The objective of this PDU was to evaluate the feasibility of such a process in developing countries taking into account the small size of factories and the low quantity of fleshings available on each site.

Various analytical tests were carried out in Indian tanneries to determine the main characteristics of the available fleshings.

Parameters	Range
Moisture content	from 80 to 91 %
Dry solids	from 9 to 20 %
Volatile solids on dry matter	from 51 to 80 %
Ash content on dry matter	from 20 to 49 %
Grease content on volatile matter	from 7 to 29 %
Protein content on volatile matter	from 71 to 93 %
Grease content on dry matter	from 3.5 to 23 %
Protein content on dry matter	from 36 to 74 %

The quantity of grease that could be recovered is very limited compared to developed countries ratio. In Europe, for example the main interest of fleshing process is connected to the quantity of recovered grease, as the price of this product is 5 to 10 time higher than the price of the protein. With different economical conditions in developing countries, this could not be the same and availability of proteins for feeding chicken can be reduced. Proteins from hide and skins can compete with fish proteins for example.

An evaluation of a full size plant was made for a tannery having 1.5 t/day of wet fleshings and 0.5 t/day of trimmings. The price of such a plant was estimated at a level of 150,000 US\$ with a cost of recovered products representing only 80 % of the processing cost. In these conditions, where disposal costs are not considered at a very high level, this type of process can only be justified with a processing of 6 to 7 tons per day of fleshings.

Evaluation of existing technologies was also prepared in the frame of this PDU. The main subjects studied were the following :

- tannery fleshings used as a source of animal protein in poultry feed formulation,
- tannery raw trimmings and lime fleshings used as a source of raw material for a glue/technical gelatine plant,
- establishing a dog chew manufacturing plant using raw hide trimmings and limed splits of hides,

For each of these treatments a document was prepared with the specification of the process and of the equipment. A material balance is included in the document. It

contains also an evaluation of the investment cost and of the running cost, with the payback time for the minimum size of the plant.

Conclusion

Various sources of waste have demonstrated that the quantity of the recovered products is highly dependant of the quality of the waste. However the available quantity to be processed needs to be at a correct level to give a minimum of profitability to the investment.

3.6. PDU/6 Mechanical desalting

Sodium chloride is widely used for preservation of raw hides and skins in South East Asia. In order to have an optimum conservation, salt content should be around 20% of the fresh raw hides and skins. It contributes to high total dissolved solids (TDS) in the soak waste liquor. TDS is a major pollution problem that cannot be processed easily as there is not yet a commercially viable technology for treatment of TDS in the tannery effluent. A substantial quantity of salt sticking to the surface of hides and skins can be removed by shaking the hides by mechanical or manual means.

The objective of this PDU was to demonstrate the interest and demerits of different salt recovery options on raw hides/skins in developing countries tanneries including the reuse of the salt for pickling operation.

Three ways were mainly tested: manual desalting on a wooden frame, mechanical desalting in a drum and using a brushing machine.

It has been also observed that, comparatively to mechanical desalting, manual operation could give, at least, a similar effect. A simple dome wooden frame called DODECA was developed for manual desalting. From the comparative study of performance by both the methods, it was evaluated that the manual desalting is a better option for Indian tanneries processing small hides and skins.

When manual desalting is adapted to small size tanneries (less than 5 tons of raw hides/skins processed per day), mechanical desalting is much more interesting for larger size tanneries, but recovery equipment needs to be adapted. Perforated wooden drums are adapted to South East Asia constraints, but stainless steel inclined cylinder, similar to those manufactured in Italy are well adapted to the opening and the handling of the hides. In India with a perforated drum, 3 to 8 % of the salted raw hides/skins weight was eliminated as dusted salt under the drum. The major quantity was obtained with buffalo hides and the lowest one with goatskins.

Comparative test carried out on the same type of hides/skins have given an average recovery value of 5 % of dusted salt by mechanical desalting and 7 % by manual operation, on the hide weight basis.

Intermediate solution such as the brushing machine can also contribute to eliminate easily up to 10 to 20 % of the salt used for curing.

Mechanical desalting drum could be efficiently used for buffalo hides and other big sized imported hides.

Dusted salt from desalting operations contains a large amount of impurities. Through dissolution in water and screening followed by clarification using polyaluminum chloride, it is possible to obtain clear salt solution. This salt solution was used in the pickling operation without any technical problem. It is considered that the remaining microorganisms are destroyed during pickling acidification and that the residual organic content cannot influence the pickling and tanning conditions.

As major result obtained, desalting operation combined with salt reuse in pickling, reduces TDS in the composite wastewater from tannery to the extent of 20-30%. However it must be taken into account the sludge produced during salt purification.

It has been observed that tanners prefer manual desalting as handling of hides and skins is limited with manual operation and no energy is required. DODECA wooden frame is widely used today in the South Indian tanneries because it is a cheap way for hides/skins desalting. Tamil Nadu Pollution Control Board has recommended this equipment as one of the methods for desalting. However, as it is not so simple to recover the used salt and it may present some risks, dumping of the residual salt needs to be controlled.

Conclusion

It should be recommended to control the use or the dumping conditions of the dusted salt in tanneries operating wooden frames or mechanical desalting.

When manual desalting is adapted to small size tanneries (less than 10 tons per day) processing skins or small hides, mechanical desalting is much more interesting for large size tanneries, but recovery equipment needs to be adapted and stainless steel inclined cylinder manufactured in Italy are well adapted to the opening and the handling of the hides. Manual desalting conducted to the creation of locally produced equipment adapted to the objective.

Desalting hides and skins is a good way to contribute to the reduction of the salt pollution, mainly in hot climate where availability of good quality water is limited.

The low quantity of salt recovered compared to the high TDS problems urges on looking at alternative curing methods for hides and skins.

3.7. PDU/7 Landfill model site

Melvisharam model site

This site was established according to the up-to-date state of the art for a capacity of more than one year of sludge production at the Melvisharam CETP. Plastic lining between clay layers was used to prevent any leachate to enter in the soil and a drainage system was established to collect rainwater coming from the site. To prevent the sliding of the clay layer, the inside slopes of the landfill site were covered with a plastic film plus a clay layer of 10 cm and a layer of 5 cm of reinforced concrete. After one year of utilisation, no cracking of this concrete layer could be seen. The access road to the deposit was completed with stone pavement in order to prevent damages with trucks outside and inside the landfill deposit. Grass is growing on the external slopes of the access road.

The site is now filled with 35 to 40 % of its capacity in sludge. The feeding is conducted in normal conditions, from the ramp inside the landfill site and from the top of the site, close to the ramp. According to the managing director of the CETP, taking into account the present production of the tanneries, the site will be used for two more years. This site is a very good example of what could be done in South East Asia to store tannery sludge in safe conditions.

Ranipet model site

Three concrete cells were created to store the sludge production from the Ranitec CETP. These cells are now full of sludge and covering was set up on the three cells, with a plastic and clay layer. As soon as the covering was completed, the tightness of the system was demonstrated as no leachate was coming from the cells.

A new landfill site is been established to store about 30,000 m³ of sludge. This site is prepared on the free area located behind the model sites already closed. The soil is excavated on 1.5 m depth and is used to build the sides of the cell. A clay layer of 30 cm will be spread on the bottom of the landfill site and at the top of the cell when it will be closed after filling. A clay layer of 15 cm will be put on the sides of each cell. Then a total capacity of 30,000 m³ will be created on a total area of 12,000 m² to contain the sludge produced in the Ranitec CETP. A fishpond exists close to the ground devoted to the new landfill site. As many fishes can be seen in this pond, it will be used to test the tightness of the new landfill site.

Conclusion

The objective of this PDU was to show that landfilling of tannery sludge is not only dumping. Location, construction, operation and even closure of the landfill have to be done under specific conditions. The objective has been achieved through:

- The edition of a manual on sludge landfilling with typical design, cross sections, leaching problems and monitoring.
- The establishment of two model sites in Ranipet and Melvisharam for disposal of tannery sludge.

Melvisharam model site has demonstrated its ability to store sludge in safe conditions, when Ranipet model site, using larger concrete quantities, cannot be considered as a model site at the same level. However it demonstrated its safeness for sludge storage. A new industrial storage site in Ranipet has been extrapolated from the two experiments.

However, it must be taken into account that controlled landfilling is a temporary solution as sludge contains an important part of organic material that needs to be recovered through various non polluting routes such as composting, biomethane production and controlled incineration. In Europe, the increasing difficulties for opening new landfill sites is strongly limiting the future of this technology.

3.8. PDU/8 Sludge composting

Shafeeq Shameel tannery

This tannery has already prepared large quantities of compost using tannery sludge and other vegetable materials. The normal piling process lasts for 60 to 70 days with 5 turns of the pile. The harvesting of the pile gives the possibility after filtration to recover nearly 80 % of the material being used during the process. The coarse product is again reused in the next cycle. This compost was analysed and the quality is considered as good.

Another system of composting is also used and a new pile of 10 m³ was just started. The aeration is obtained by suction with a ventilator. It seems however that the humidity of the pile is drawn by the aeration system and can lead to a fast drying of the pile. Humidity is however controlled with the addition every day of water on the sides of the pile. Normally with this system, the operation time is shorter (about 40 to 45 days), but two mixings are still needed. This could be due to the difficulty to have a good mixing at the beginning of the composting operation.

With this suction system, the pile is enclosed in a kind of big box with three concrete walls 1.5 m high and a closure is done with wooden planks. The suction pipes with holes are located at the bottom of the compartment and the air goes across the pile. The permeability of the pile is very important to let the air distributed everywhere. It is not necessary to try to reduce the coarse materials because they bring permeability of the composting pile and they are reused one or several times.

At Shafeeq Shameel tannery, the compost is used for growing cotton. An experiment was started with two equivalent areas planted with cotton. In one of the fields, the cotton is irrigated with secondary treated effluent. In the other field, besides irrigation with tannery effluent, some compost was used to plant the cotton. The result obtained is highly interesting as the production of cotton increased by 100 %. Instead of the normal production of 200 kg/ha, the first results demonstrate a production of 400 kg/ha. The plants look bigger and the density of cotton is higher. The harvesting of the cotton (three times in a year) will be continued to verify the first results obtained.

Another experiment is pending to grow castor-oil plants to produce seeds yielding lubricant oil. A third experiment will be conducted to grow silk-cotton trees.

SIDCO experiment with vermi-composting

The total area devoted to composting is now 100 m² and the production is around 4.8 tonnes per pile with a total of 8 piles, with 4 tonnes of dried sludge, and 600 to 800 kg of cow-dung and around 100 kg of leaves from the mini-forest. The number of worms introduced in each pile is in between 2800 to 3700. Average cycle time is 70 days and the worms are introduced after 20 to 30 days in the pile because of the slight increase of the temperature (40 to 45°C). The yield of fine compost is 92 %. Organic carbon at the beginning has large variation from 10 to 40 % giving an organic matter of 18 to 72 %. At the end of the process the organic carbon ranges from 7.5 to 15 % and the organic content from 13 to 26 %. The average nitrogen

content in the sludge is 0.95 % at the beginning and 1.35 % in the final product. Phosphorus is 0.25 % in the inlet and 0.38 % in the final product.

MAKH tannery

Since April 2000, MAKH tannery is operating every day about 4 tons of dried sludge mixed with other wooden materials in the ratio 66 % sludge and 33 % other products to manufacture some compost. The structuring product is mainly constituted of pieces of wood or small branches that can be reused several times in the composting process.

The piles are established for 70 to 75 days with 4 to 5 turns. The highest temperature (65 to 70°C) is normally obtained after 4 days and 10 to 15 days are necessary to gradually reduce the temperature up to 60 – 62°C. Then the pile is turned and the temperature increases. Already 70 tons of compost have been produced, put in bags and sold or given for plantation at Ranipet CETP.

Conclusion

These various tests, carried out for some of them with a very limited investment, have demonstrated the feasibility of the composting process with tannery sludge and structuring vegetable materials giving to the air the possibility to enter into the pile. They are now operated on a continuous and commercial basis. Piling system, with turning every 4 to 5 days, is the most commonly used system. However, large piles with air suction equipment can be used to delete the turning of the pile and have a better control of the parameters of the process (temperature, humidity). Vermi-composting is also a good practical solution to delete the turning of the mixture.

According to Indian regulations, as soon as the sludge contains less than 5 g/kg DS of chromium, it is possible to use it for composting process. However this compost should only be used for non-edible crops. In France, for edible crops, the maximum permissible limit for chromium is 150 mg/kg DS.

3.9. PDU/9 Irrigation

SIDCO experiment

The mini-forest in SIDCO is growing in good conditions in the places where the soil was not too much polluted by saline effluents. In the other places, growing is slow for the moment. For assisting new plantations, in these places, some compost or vermi-compost could be used. The best growing observed is for eucalyptus, followed by mangium. The observation of the salinity in the ground water confirm that after a notable increase, before monsoon period, the salt concentration decreases and is again the same after monsoon period. New figures up to end of December will give the possibility to establish a kind of mass balance. Values for chloride, which were missing at the middle of 2000, demonstrate the same variation as TDS.

After checking all the results available for 1999 and 2000, (figures are annexed in Excel format) it seems that there is a slight decrease of 4.4 % in the first level of the

ground water at 6 feet, but also an increase of 7.6 % of the parameters in the deep level of the ground water at 40 feet. These points can be seen on the mean values for each month at eight different piezometer points, four at 6 feet depth and four at 40 feet depth.

Parameter	TDS mg/l		Chloride mg/l		Sulphate mg/l		Total hardness mg/l		EC mmhos/cm	
	6 ft	40 ft	6 ft	40 ft	6 ft	40 ft	6 ft	40 ft	6 ft	40 ft
Mean value	6 401	3 065	1 389	658	1 420	923	2 372	1 640	9,8	4,7
Variation 2000/1999	-1.5%	3.8%	2.0%	6.8%	-1.9%	20.5%	-19.3%	3.0%	-1.5%	3.8%
Mean variation	1.2%		4.4%		9.3%		-8.1%		1.2%	

Looking at the different parameters, if TDS is slightly decreasing by in the upper part of the ground water, it is increasing in the lower part. More problematic is the increase of chloride in both level of the ground water. The same phenomenon is taking place for sulphate but with much higher increase in the lower part of the ground water. Total hardness is the only parameter to be reduced, but it is increasing in the lower level of the ground water. Electrical conductivity has strictly the same variation as TDS.

It could be said that the lowest quantity of rainwater in 2000 (430 mm in Vellore compared to 850 mm as average value for the 4 last years) has some part of responsibility for this increase. However as the irrigation process is responsible for more than 80 % of the water arriving on the planted area, some serious control is to be continued to be sure that no stronger increase occurs.

Attempt at mass balance in Sidco mini-forest.

Average effluent coming from Sidco CETP and sent to the site:

	Concentration	Kg/day	Tonnes/year
TSS	118 mg/l	81	30
TDS	4225 mg/l	2916	1064
BOD ₅	22 mg/l	15	6
COD	281 mg/l	194	71
Chloride	568 mg/l	392	143
Sulphate	1745 mg/l	1204	440

This represents 236 tonnes of sodium chloride and 650 tonnes of sodium sulphate every year.

- Effluent received: 690 m³ per day or 252,000 m³/year with 143,136 kg of chloride (568 mg/l)
- Rain received on the site: 850 mm/year on 37,000 m² = 31,450 m³/year
- Total effluent + rain: 283,450 m³/year with 143 tonnes of chloride (505 mg/l)

It is estimated an absorption and evaporation rate of 20 %, taking into account the observation made on reed beds (PDU/1).

The effluent and rain evaporated will be: 56,690 m³/year.

Effluent and rain sent to the ground water will amount: 226,760 m³/year with 143 tonnes of chlorides (644 mg/l).

Theoretical assessment

Additional surface needed for irrigation

To maintain the same level of chloride in the ground water, an extra surface must be planted for the same quantity of effluent:

$$252,000 \text{ m}^3/\text{year} - 226,760 \text{ m}^3/\text{year} = 25,240 \text{ m}^3/\text{year}$$

This extra rainwater will be collected on an increased surface of:

$$25,240 \text{ m}^3/\text{year} : 0,85 \text{ m (850 mm/year)} = 29,700 \text{ m}^2 \text{ or } 7.4 \text{ acres}$$

that is to say a total surface of 37,000 + 29,700 = 66,700 m²

Reduction of effluent to be sent for irrigation:

To maintain the same level of concentration, rainwater must compensate the evaporation.

- Rain water: 31,450 m³/year
- Total water to be sent: $31,450 / 0.20 = 157,250 \text{ m}^3/\text{year}$

This quantity represents an average volume of:

- $157,250 / 365 = 430 \text{ m}^3/\text{day}$ out of the daily effluent 690 m³, that is to say, only $430/690 = 62 \%$ of the daily effluent coming from the CETP.

Practical assessment

Taking into account the real values observed on site, it is possible to see that the highest impact is for sulphate at the depth of 40 ft with an increase of 20.5 % of this

parameter. It is then necessary, either to reduce the volume to be delivered to the site by 20.5 %, or to increase the surface of irrigation by 20.5 %.

Taking into account the situation of both the higher and the lower level of the ground water, a decrease of the effluent volume or an increase of the irrigated area by 9.3 % is necessary.

For TDS, the respective values are 3.8 % reduction of volume or 1.2 % reduction in volume.

For chloride, the respective values are 6.8 % reduction of volume or 4.4 % reduction of volume.

Ranipet CETP

In order to evaluate the possibility to use highly saline effluent for irrigation, some test will be carried out within the CETP. The model of the plantation uses ridges and furrows to keep the salinity out of the roots of the plants. The accumulation of salt at the bottom of the furrows will be a good test for prevention of TDS increase in the soil.

More than 3000 trees are being planted on 24,000 m² and the plantation is using the compost prepared with tannery sludge at MAKH. A total of 750 m³ of tertiary treated effluent will be delivered every day in the plantation area.

Conclusion

The various tests carried out at Sidco CETP have demonstrated the feasibility of irrigation of trees with treated tannery effluents containing limited quantities of TDS. However, some controls have to be done regularly in piezometers in order to evaluate the long-term incidence on the quality of the various layers of ground water. After two years of experiments, the TDS increase in the deep ground water is slightly positive. This will need some further controls to confirm this aspect. Then some changes in irrigation practices will be necessary.

In any case, this experiment has brought the possibility to demonstrate that a degraded land can be rehabilitated with trees plantations irrigated with tannery treated effluents.

3.10. PDU/10 Enzymatic treatment of shavings

The first tests started at CLRI under the supervision of Prof. Karel Kolomaznik from Technical University Zlin in Czech Republic. We visited the place on Friday 14 July and we had the opportunity to discuss with Mr Kolomaznik.

The report prepared by Prof. Karel Kolomasnik after the test carried out in 2000 in India at CLRI presents the technology adopted. This technology uses organic amines and magnesium oxide for the first step and proteolytic enzyme in the second step. The filtered chrome cake is acidified and used for the preparation of a tanning chrome liquor. The clear solution of hydrolysate can be concentrated and dried. Many applications can be found for the hydrolysate or gelatable protein in agriculture, building and plastics, resin and rubber industry.

For European countries, the main limitation of the process is the energy requirement for the concentration of the protein solution, but it is possible in India to find some specific and cheaper solutions. On another hand, in the production of gelatble proteins, n-butyl amine represents 75 % of the cost. Replacing this product by MgO, the cost can be cut by half. For one ton of shaving, the processing cost reaches 250 US\$ and the market for the recovered products needs to be developed.

3.11. PDU/11 Oxidation ditch in Ambur

Oxidation ditch is a very good technology for biological tannery effluent treatment. In order to demonstrate the feasibility of such a project in Asian country, it was decided to upgrade the existing oxidation ditch in Ambur Thuthipet CETP, one of first CETP built in Tamil Nadu. CTC objectives were to control the technical design and to discuss the various technical options for Amburtec.

The main improvements to be carried out in the first phase were as follows :

- Replacement of raw effluent pumps.
- Installation of two manually cleaned screens prior to equalisation tank.
- Providing adequate mixing/aeration capacity (60 kW/hour as calculated as the necessary mixing power) besides demolishing the baffle wall in the equalisation tank.
- Providing suitable flocculation mechanism besides improving the existing clarifier mechanism.
- Improvement of the operation of the pre-aeration tanks.
- Improvement of aeration in oxidation ditches by installing suitable vertical shaft aerators.
- Construction of an additional secondary clarifier
- Improvement in monitoring by providing flow measurement, DO measurement, etc.
- Improvement in management and monitoring of the CETP.

This programme was discussed with RePO in Chennai, with TEH Projekt, the main consultant involved in the technical rehabilitation, with the management of the CETP and with UNIDO Vienna. Several visits on site were organised to confirm all points to be taken into account.

When checking the latest results obtained with the newly equipped oxidation ditches, it is certain that the equipment installed has good performances. Only a few remarks can be done.

- The running time of the aerators seems too high, as the outlet quantity of dissolved oxygen is very high, sometimes higher than 5 ppm. Then there is wastage of energy. A value comprised between 1 and 2 ppm in the oxidation ditches is sufficient to ensure a fast elimination of residual sulphide if any. A higher value will not bring better results and will limit the nitrification denitrification effect in the ditches. From the latest results in January, it can

be seen that the highest DO in outlet correspond to the lowest quantity in effluent to be processed every day. Then the aeration time could be related to the volume processed per day (checking the pumping time to the primary settler). However the best economical solution will be to adjust the aeration time to the DO measurement in oxidation ditches.

- Sludge volume index in the ditches is good and it must be preferably below 150 ml/g.
- Every day, 25 m³ of bio sludge is extracted from the secondary clarifier and sent to equalisation tank for mixing with primary sludge. This quantity could be reduced in order to increase the biomass in the ditches. The concentration of MLSS seems low. No data is available of the MLVSS that could give good indications on the biomass being present in the ditches. A value of 3 g of volatile suspended solids could certainly improve the results already obtained.
- Results of analysis show a strong increase of TDS in effluent from 7000 mg/l in January 2000 to 14000 mg/l in January 2001. The explanation given is related to the increase of TDS in the ground water. However 100 % increase has certainly another explanation. Ammonia nitrogen increased in July, August, September and October, and no value are given for the last four months. Some change in hides and skins processed in the tanneries with more raw hides and skins could be one of the reasons of such an increase in TDS but other reasons such as analytical problems can be foreseen.
- Analytical results show that some sulphide is present in the outlet of the plant after biological treatment. This is quite surprising as the DO level is always higher than 1.5 mg/l (during the month of October). It is also quite surprising to have, for some months, no sulphide and in April, May and October very high figures such as 148, 48 and 40 mg/l respectively. If these results were obtained by TNPCB laboratory, the preservation of samples before analysis must have been too long in warm conditions and some sulphite or hyposulphite turned back to sulphide in anaerobic conditions.

Conclusion

The Ambur CETP is now a model plant with an excellent upgradation of the existing oxidation ditch. Some more work is still pending to adjust the running of the plant to the load received. It is only regrettable that a tertiary treatment was implemented before the improvement of the secondary treatment and this tertiary treatment is now useless.

3.12. PDU/12 Improvement of conventional chrome tanning

About 80% of the Indian tanneries are using chrome tanning process. Chrome tanning is done in traditional wooden drums with capacity to process about 1 ton of hides. In conventional chrome tanning, on average, the leather takes only 60% of the chromium applied in the form of Basic Chromium Sulphate (BCS) and the remainder discharged as waste in the effluent. Poor mechanical driving system, improper feeding arrangements for chemicals and water etc. and leakage through

door and other parts of the drum lead to big waste and reduced uptake of chemicals. The pH and float also have to be properly controlled.

High concentration of chromium in the tannery effluent signifies a big loss and an environmental hazard. It complicates the treatment and increases the cost of treatment. Disposal of chromium containing sludge costs more as, in many countries, such sludge is regarded as a hazardous waste.

The objective of this PDU was to demonstrate that the chromium uptake by leather can be increased up to 75-80% by improving the chrome tanning wooden drum at low cost and by better process control without any change in chemical input. This improvement will result in better quality of wet-blue, savings in chemicals and overall reduction in chromium wastage including from washings and leachate.

In view of these expected advantages, an existing wooden chrome tanning drum (2.4 X 2.4 m) in Delta Leathers tannery at Ambur was improved and the parameters that influence the chromium uptake were studied for a period of 6 months with a total of about 70 full scale trials for optimisation.

The first phase of the PDU consisted in improving the chrome tanning drum on the drive arrangements to incorporate variable speed (6 to 12 rpm), forward and reverse rotation, timer control for forward reverse rotation, improved door arrangement to stop leakage and improved drainage arrangement.

The following parameters were identified for regular monitoring for every batch of operations carried out after implementation of the improvements to the selected drum on batch basis.

- Pelt weight.
- Residual float from pickling.
- pH of leathers before addition of chromium.
- Quantity of chrome powder/chrome syntans used.
- Duration of process with break-up in feeding.
- Quantity of fresh water added during basification.
- Quantity of sodium formate used.
- Quantity of sodium bicarbonate used.
- Temperature of the float (Initial and final).
- Total float including pickle float and float added during basification.
- Duration of basification with break-up in feeding.
- Final pH of wet-blue leathers.
- Final pH of float.
- Chrome content in wet-blue processed.
- Chrome content in spent chrome liquor.

- Percentage of uptake of chromium.
- Power consumption during each operation.

After 70 trials, the optimum parameters for chrome tanning were determined as follows:

Speed of the drum	10 rpm or 1.19m/s peripheral velocity
Total float including pickle float and basification	100%
Pickle float in percentage based on pelt weight	70%
Total duration of drum operation	4 h 30 mn
Duration of chrome tanning before basification	2 h 45 mn
Duration of basification	1 h 45 mn
No. of feeding of chromium	Minimum of 2
Characteristics of pickle float	pH: 2.7-2.8, Chloride content: 70 g/l.
Application of BCS	7%

Conclusion

The tannery where these trials were implemented already decided to carry on the improvement for other tanning drums in order to obtain the same quality for the whole leather production. Taking into account the additional power cost for the drum motor, maintenance, financial costs and depreciation, savings in chromium sulphate are estimated at 3000 US\$/year and savings for spent chrome liquors at 660 US\$/year. The improvement of chrome tanning for one drum brings a net annual profit of 1840 US\$.

It is however regrettable that the replication of this PDU was not done more widely as the interest for tanner is evident. An explanation could be brought with the low quantity of chromium used in tanning in many tanneries (about 4 % BCS) and the high quantity used in retanning (4 % BCS or more).

3.13. PDU/14 Solidification of sludge

As a rule of thumb, the amount of sludge (dry matter) generated is approximately:

- 10 % of the total weight of skins processed (goat and sheep)
- 14 % of the total weight of hides processed

150,000 of partially dried (50 %) sludge would be generated by ETPs and CETPs if all Indian tanneries treated effluent.

Sludge from tannery effluent treatment plants in India has been categorised as hazardous waste (category 12) because of its chromium content.

The main objective of Solidification and Stabilisation (S and S) technology is to convert the hazardous and toxic wastes into an inert, physically stable mass with very low leachability.

Results obtained

Mixtures of soil and sludge in various proportions for each of the CETP sludge were tried.

3 CETPs sludge were tested :

- RANITEC CETP, Ranipet
- SIDCO CETP, Ranipet
- VISHTEC CETP, Melvisharam

These 3 CETPs generate 23 tons of sludge per day (dry matter basis).

Different admixtures were tested and the chemical properties, i.e. non leaching of chromium, were good with all these experiments. Physically, the bricks produced gave the following results, listed in rank order best on top:

1. Wet sludge + brick day + sand
2. Pulverised sludge + cement
3. Pulverised sludge + brick clay + fly ash
4. Pulverised sludge + brick clay
5. Pulverised sludge + clay soil
6. Pulverised sludge + fly ash + lime
7. Wet sludge + wastes from ceramic industry

Conclusions

Satisfactory results have been obtained on locally made bricks. Evolution of the bricks versus time has not been tested. It is not known what would be the evolution of the chemical and physical properties of the bricks. Therefore, CTC recommends not using the bricks for construction. The stabilised sludge can of course be used for landfilling (India considers tannery sludge as hazardous waste when it contains more than 5 g chromium per kg DS) and as road material. This should, of course, be discussed with the local authorities.

3.14. PDU/15 Evaporation of effluents

Raw hides and skins in Asia are mostly preserved with salt (sodium chloride). The resulting washing floats and the various inorganic chemicals used during leather processing bring large quantities of total dissolved solids (TDS) in tannery waste water. The resulting concentration of TDS in global effluent from tannery is comprised between 5,000 and 15,000 mg/l and these TDS cannot be eliminated

through classical waste water treatments. Two ways are only possible to recover the water separately from salt, either membrane technology such as reverse osmosis, or artificial evaporation. Natural evaporation, used in hot countries, cannot give the possibility to recover the liquid phase. Membrane technology is tested under PDU 2.

The objective of this PDU was the evaluation of artificial evaporation for processing tannery effluents.

Results

If the objective is the recovery of desalted water, various evaporation technologies are available:

- single and multiple stages evaporation,
- evaporation with thermo-compression where compressed steam is reused to increase evaporation efficiency,
- heat pump assisted evaporation,
- freezing of the mixture and separation of desalted ice.

When comparing the energy requirement in kWh per tonne of processed water, the following table is obtained:

	Energy required in steam	Energy required in electricity	Total
single stage	921 kWh	20 kWh	941 kWh
multiple stages (5)	192 kWh	6 kWh	198 kWh
thermo-compression	173 kWh	16 kWh	189 kWh
heat pump	0 kWh	70 kWh	70 kWh
freezing	0 kWh	17 kWh	17 kWh

As freezing and heat pump are mainly adapted to pure saline effluents, multiple stages evaporation systems can be used for brackish water.

Multiple stages evaporation can be considered as a possible option for saline effluents. To implement a 5-stages system, 4 crystallisators, 2 condensers, 1 fresh steam trap, 4 secondary steam trap, 1 crystallised salt settling tank, 1 vacuum system for uncondensed gases, 1 steam boiler (1 ton steam, 15 bars), 1 air cooling for water and required pumps are needed. This equipment is fitted to 1000 m³/day of water containing 15 g/l of TDS (12.4 g/l of sodium chloride).

This system needs to be built in corrosion resistant materials and estimated cost for such a system cannot be estimated easily as it needs to be built to specific order. However the energy consumption can lead to evaluate the overall cost of such a system to about 4 US \$ per m³ of water, for a unit size of 1000 m³/d.

Conclusion

This multiple stage evaporation system (or mechanical compression system) is an ultimate solution when the complete recovery of water is needed. Furthermore, the

efficiency of the system is independent of the salt concentration and it can compete with reverse osmosis costs for salinity higher than 15 g/l and no residual liquid is to be processed. Compared to reverse osmosis, this system appears to be more expensive, but it minimises the reject obtained and maximises the possibility to reuse tannery effluent compared to any other system.

This point was discussed with the managing director of the CETP in Vanyambadi. The board of the CETP wishes to have a clear idea of the investment for the installation of a multiple stage evaporation system, as it appears that no improvement can occur in the quality of the ground water if no effort is done to reduce the salinity of the effluent coming out from the CETP. They are expecting that, within a few years, authorities may enforce such a treatment. Compared to usual costs of water treatment in Europe, an additional evaporation system would not create a significant disadvantage in South of India for tanners.

It is highly remarkable that tanners have a medium term view to improve the existing situation regarding the quality of the ground water and some assistance could be brought to this CETP in this matter.

3.15. PDU/16 Improved solar evaporation

In Tamil Nadu and in Southern States of India as per pollution control regulations the tanneries are required to segregate the salt laden soak and pickle liquor and discharge into solar evaporation pans. Soak liquor at the rate of 5 to 8 m³/ton of raw material processed is discharged into solar pans. These pans occupy large land area constructed at the prescribed average rate of 220 m² per m³ liquor discharged per day. In addition to the large land area required for evaporation the settleable and other impurities in the soak liquor not only slow down the evaporation process but also the recovered dry matter contains a large percentage of impurities along with the salt.

The objective of this PDU was to improve the evaporation rate from the average level of 4.5 mm/day to 10 to 15 mm/day and to obtain comparatively better quality of salt from the solar evaporation pans.

The basic principle of the augmented solar evaporation system includes removal of suspended and colloidal impurities with physico-chemical treatment. It also improves the evaporation by thermo-dynamic action. A pilot demonstration unit for 5 m³/8 h capacity was implemented at Shafeeq Shameel & Co., Ambur by UNIDO with the technical support of the Indian Institute of Technology, Madras, as the subcontractor.

The pilot plant comprise of screen chamber, collection tank with 6 m³ capacity, hopper bottom settler with 2.5 m³/day capacity, 80 m² RCC platform at height of 3 m for providing black plastic sheet at 13° slope facing south for solar warming and sprinklers numbering about 120.

After test and trial operations the system was working satisfactorily from December 1998. The overall evaporation rate was increased by 150-200% compared to the evaporation rate in conventional evaporation pans. After solar warming and sprinkling the concentrated saline solution (TDS at 100-110 g/l) is discharged into

shallow pans at a depth of less than 4 cm. Salt crystals were formed in a period of 5 to 6 days.

Further studies in optimising the evaporation, further clarification of the concentrated saline solution to obtain better quality salt, reuse of concentrated saline and recovered slat for pickling were tested.

The smell during aeration is minimum since the soak liquor is clarified daily and stored in shallow open pans with a height less than 15 cm.

Some continuous tests were carried out in Shafeeq Shameel tannery with the existing equipment. The main difference with the previous tests is that the operation is going on a continuous basis and the sprinklers are used up to a concentration higher than 200 g/l of sodium chloride, giving a residual volume of 20 to 25 %. Then the concentration obtained is between four to five times. At this concentration, the sprinklers start to clog and the pumping is stopped. Sodium chloride obtained in the evaporation pond after concentration is reused for pickling as the shape of crystals makes it difficult to reuse for salting of hides and skins. The high concentration of sodium chloride obtained justifies the test and it can be said that the saving in space is high with the results obtained during the last four concentration cycles.

New plant at ATH tannery

A new installation is being set up at ATH tannery for processing soaking effluent. The new plant will process about 20 m³ per day on a surface of 465 m² (2 areas of 31 m x 7.5 m) equipped with a sprinkling system constituted of pipe distribution with a total of 360 sprinkling points with 1.5 mm opening located at 1.2 meter over the collecting area. During a demonstration with clear water, each jet was sprinkling higher than 3 m.

The soaking effluent is stored in two 10 m³ tanks and treated with polyaluminium chloride and polyelectrolite before been delivered to a 20 m³ settling tank. Sludge is eliminated and the settled effluent passes through a sand filter before the final storage. Centrifugal pumps are used to distribute the effluent through the piping system. Recirculation is assumed on a floor in concrete with a slope directing the effluent towards the pumping system. Operations could start within one week that is to say by the 8 or 9 February.

The cost of the equipment is 126,000 Rs for the pumps, 79,000 Rs for pipes, fittings and valves. An extra cost of 33,000 Rs is foreseen for the nozzles if the holes cannot match the required size.

Conclusion

The principle of the system is good and the replication already installed at ATH confirms the interest of tanners for such a system. The tests been carried out at Shafeeque Shameel tannery must confirm that the savings of evaporation space compensate widely the investment and the running cost involved in such a system.

A ventilation based system is now under development in France with higher possibilities of saline water evaporation per m². The system is based on a laminar packing - a pad - in the form of honeycombed panels. It is made of High Density Polyethylene. Its shape optimises natural evaporation. Due to its high void index,

200 m² of exchange surface are available for 1 m³ of pad. The mechanical ventilation used is equivalent to a constant wind speed of 4 m/s. The spraying system ~~is spraying~~ ^{High density Polyethylene} the liquid, from the receiving tank on the wire mesh, producing regular cycles of evaporation and concentration. A part of the liquid is evaporated, and the rest sent back into the receiving tank.

This system was tested with a brine liquor coming from a hide preservation unit. Starting from an effluent containing 162 g/l of chloride, it was possible to reduce its volume by 60 %, to obtain a residue with nearly 400 g/l of chloride. For soaking effluent containing 30 to 50 g/l of chloride, it could be possible to concentrate it by ten times without any clogging of the system. Taking into account the area of the system, the evaporation rate could be as high as 75 mm per day (nearly 17 times the natural evaporation rate observed in the Chennai area). For the evaporation of 1.12 m³ per day, the energy requirement is 72 kWh in European conditions.

This equipment could be tested in India.

4. INDIA phase 2

4.1. Output 1- Low waste environmentally acceptable leather finishing operations

The main conclusions of the work done in India on this subject confirm the poor controls on floats volumes, floats temperature and uptake of chemicals. It shows that a lot of TDS is brought though the use of some specific chemicals such as neutralising and retanning agents and also dyes. Another point to be noted is the poor biodegradability of some chemicals in post-tanning operations. For example, if COD and BOD₅ are compared, for some used floats, the ratio COD/BOD₅ is often higher than 4 and sometimes reaches a higher value. In Coromandel leathers, the COD/BOD₅ ratio for dyeing and fatliquoring waste liquors is over 23. In these conditions, biodegradability will be poor during biological treatment of effluent and the residual COD obtained in the final effluent from the CETP or ETP will be high.

Facing this problem, a survey of the biodegradability of the main products used in post tanning operations could give the possibility to tanners to select biodegradable products, for example pyrogallic vegetable tannins instead of pyrocatechic products, syntans, fatliquors and dyes having a good biodegradability. Measurement of the biodegradability could be obtained with the ratio: $\frac{BOD_{20} - BOD_5}{BOD_{20}}$. If this ratio has a

value near zero, the substance may be either totally biodegradable within five days or not biodegradable even in long term, if COD/BOD₅ is higher than 4. If the ratio has a value near one, the substance is biodegradable, but slowly. Extensive type biological processes will be required and the rate of biodegradation that could be achieved may be calculated with a BOD corresponding to the contact time of the biological step.

The work presented in the final report of this subject is very interesting as it shows that simple measures can improve the situation in post tanning operations. The main recommendations can be summarised as follows:

- Measure exactly the quantity water used in the processes
- Ensure that excess quantity of water is not used in any operation
- Uptake of the chemicals viz., chromium in rechroming operation, syntans, dyes and fatliquors can be obtained by initially allowing the chemicals to penetrate into the leather and then fixing them. To make the fixing uniform throughout cross-section and surface of the leather, further float can be added.
- During wetting back maximum of 200% is sufficient.
- For washing operations float of 200% is sufficient.
- In rechroming operation the maximum uptake of chromium can be obtained by starting the operation at low float and after complete penetration of chrome further float is added to fix the chromium. The maximum float for rechroming is 100%.
- Neutralization operation should be made to equilibrium i.e. through out the cross section of the leather. This could be obtained by extending the duration of the operation. This should be done carefully to avoid grain looseness.
- In retanning operation maximum float is 100%. In this operation also float can be started at minimum and increased at the end of the operation before fixing.
- In dyeing operation float should be kept at minimum of 100% in light coloured leather to make uniformity in colour throughout the surface of the finished leather. For dark coloured leather the float can be reduced even below 100%.
- For final rinsing maximum float of 100% is sufficient. The excess quantity will leach the chemicals fixed in the leather.

It should be also added that some recipe can be simplified and in some cases some useless products remaining in the recipe could easily be delete after some laboratory trials. This can hardly be done in small-scale tanneries, but could be the objective of consultants from CLRI.

4.2. Output 2 - Rehabilitation & utilisation of degraded land

An investigation was carried out in the Vellore district in two places : Ranitec CETP at Vannivedu and Amburtec CETP at Periaravikam. This investigation concerned the quality of the soil around the CETP that was formerly receiving raw effluent, and the quality of the ground water. Interaction between soil and effluent was also evaluated.

This investigation gives a very good idea of the situation around tanneries in these two places. Some recommendations are given on crops species that could be grown on these two sites.

The recommendations are limited to non edible crops such as flowers, cotton and several varieties of trees such as Casuarina, Eucalyptus, Bamboo and Neem. The soils of the area surrounding both the CETPs are considered suitable for growing fruit trees such as Guava, Sapota, Annona, Jambulana and Ber. However, only non-edible crop species are recommended taking into account the precaution required to be exercised while dealing with treated effluent containing chromium and other risky elements.

The investigation on the risk for human consumption of those fruits using treated effluent needs more time and extensive field study.

4.3. Output 4 - Anaerobic digestion of sludge from soaking

In order to improve the evaporation rate of saline soaking effluent, it was demonstrated that some physico-chemical treatment could bring some positive results. The objective of output 4 was to process soaking sludge through anaerobic digestion in a UASB reactor. The equipment was ready to operate in October 1999.

The system is run in good conditions. With the gas meter, it is possible to check the daily gas production, and a manometer is used to control the pressure before releasing the gas. But a small compressor and a gas holding tank are needed if some use of the gas is foreseen. With the total volume of the gas in the tank, then it will be possible with the pressure to determine the produced volume during a fixed time.

Some sludge needs to be evacuated from the system and could be sent on sludge drying beds. On the contrary of the digestion process in PDU/4, the pH of the sludge is increased during the process. It should be interesting to measure the CO₂ and H₂S content of the gas produced. To control the effect of digestion process, it should be interesting to have an overview of suspended and volatile solids entering into the digester, in the blanket and in the final effluent.

The filter-press for sludge dewatering is operated in very good conditions in the CETP with eight cycles on a 24 hours basis. Each cycle lasts between 150 to 180 minutes. During the first 30 minutes, the sludge is fed at the maximum speed (350 rpm) of the screw pump. The next 30 mn, the pump runs at 200 rpm and for the last hour the speed is 100 rpm. The maximum pressure of the pump is 12 bars, giving a hydraulic pressure of the closure system of about 500 bars. For emptying the press, 20 to 30 mn are required and every 20 cycles, a high pressure (70 bars) cleaning of the clothes with water is required.

The Netzsch filter press has 60 chambers with 800 x 800 mm plates and a cake thickness of 25 mm. 5 m³ of sludge at 60-90 g/l are used in each cycle and 720 litres of cake are produced at a dryness of 35 - 40 %.

Conclusion

This system is interesting for processing soaking sludge coming from the soaking float treatment necessary for accelerated evaporation systems. It can also be used with sludge obtained from a chemical treatment of soaking floats sent to solar pans. However, to justify the investment and to give the possibility to recover some gas, a minimum size is requested. A gas production between 200 to 300 m³/day can be considered as justifying the scrubbing system and the generator for electricity. This implies that large quantities of soaking sludge be available at the same place. When processing 5 to 6 m³ of soaking sludge per day, the theoretical quantity of gas to be produced would be about 24-25 m³/day.

5. CETP upgradation

5.1. Ranitec CETP

The operations are going in good conditions and the quality of the equipment is improving. The two venturi aerators located have very good performance without any clogging problem. The two presettlers are producing large quantity of sludge and a pump is used to transfer one part of this sludge to the sludge drying beds located behind the biological section.

However, even with the two presettlers, the installation of a mechanical screening remains an important objective to demonstrate that it is possible to remove large particles without setting the employees in bad working conditions.

Fine filtration is operated in good conditions with a constant flow and fine particles are recovered at a high rate. No more problems occurred on the floating aerators since they were modified.

It can be noted that all the floating surface aerators (3 in equalising tank and 5 in the degasifying tank) are all running. Since this type of equipment was modified by the CETP (protection of the bearings) the breakdown are much less frequent.

Test carried out to clean the anaerobic lagoon with a screw pump were not fully successful because of the compactness of the sludge, damaging the stator of the pump. Some tests will be done with a submersed centrifuge pump hanged on a floating equipment (from a surface aerator).

The centrifuge has been operated during the monsoon period and is now stopped. A small electrical problem has to be repaired and spare part is ordered.

With suspended solids between 100 and 120 mg/l and with a BOD₅ around 60 mg/l, it was necessary to improve the secondary treatment. The overflow of the secondary clarifier was upgraded and is now flowing equally on the whole circumference. However good results are obtained only if the flow is limited to 200 m³/h, i.e. if the settling speed does not exceed 0.7 m³/m²/h. Some suspended solids are eliminated at the overflow when the quantity of water processed is higher.

Trees plantations were done recently along the tanks to improve the aspect of the plant. Original signal panels have been placed at main places of the CETP. The management of this CETP is one of the best seen in India and it is very positive that the same man will control the Melvisharam CETP.

Controls to be operated in the Ranipet Tanneries

A visit was paid to PRC Leather (Ammoor road) in Ranipet. This company was testing the flow metering system before implementation in all tanneries (76) connected to the CETP. This equipment uses a centrifugal pump and an electromagnetic flow meter for a more or less regular delivery of 12 m³/h. Before this equipment, connected to the industrial sewer, some pre-treatments were set up.

The first equipment is a bar screening system using an assembling of round and rectangular plastic bars. Although the quality of this equipment is good, it seems not really adapted to tanneries. The round form of the bars will not facilitate the cleaning of the system and will lead to clogging of this equipment. The section of the bars is too small and the bars too soft. Some material can be forced between the bars, although the theoretical spacing is 5 mm. It should be highly recommendable to use a stronger equipment made of the assembling of 316 SS bars with a spacing of about 6 to 8 mm, much more easy to clean.

Then some settling takes place in several settling tanks before the last compartment where the effluent is pumped to the sewer. If sludge needs to be eliminated before sending the tannery effluent to the sewer, it is necessary that some good assistance be provided by CETP to collect either dried sludge or liquid sludge when not enough space is available for drying. It should be better to let some sludge going into the sewer than to oblige tanner to collect some sludge and send it in an inappropriate place.

If the metering system is installed, it must not give any possibility of by-passing. This must be seriously examined before serial construction.

To reduce the load sent to the CETP, some cleaner production measures needs to be promoted. It is also highly advisable that the pollution charges be based on load and not only on volume. Then the tanner will immediately see an interest in implementing cleaner process. COD, TSS and TDS could be the main parameters to be charged. This could be obtained with a collection of flow proportional samples in connection with the flow meter. A pneumatic pump needs to be used and the sample must be constituted weekly. Every week, a controller will collect samples and will empty the collection container. These samples can be analysed randomly in the CETP laboratory.

Regarding the cost structure of the CETP and the payment according to the volume, if there is any doubt on the by-passing of some effluent in tanneries, it could be evaluated the installation of water meter on fresh water delivery lines coming from the ground water pumps.

5.2. SIDCO CETP

The new filter-press installed is running with the sludge collected at the sedimentation tank. The dryness of 35 % without any conditioning is obtained after

a three hours cycle. Effluent are mainly from wet-blue and EI to finish. The colour of the cake is brownish and no sticking effect was observed when opening the filter. The tank on wheels used for collection of the cake does not seem very well adapted to the situation although hands could displace it.

5.3. Meera Hussein Tannery ETP

This tannery was visited on 12/07/00 and this visit gave us the possibility to discuss with the managing director of the company. Since the change of the ownership of the tannery, many modifications occurred in the factory. Today they processed 6 tons of raw hides per day (Indian or Russian origin) from raw to wet blue. They have installed two large Italian drums for the process of 5 tons of raw hide. In some weeks they will be able to produce 10 tons of raw hides per day. Compared to the former production of 3 tons, the capacity of the factory will be increased by more than 3 times and the ETP cannot be used to process 150 m³/day. Today, with 6 tons per day, and 100 m³/day, a large part of the effluent is not processed, although some important modifications occurred in the biological section with the transformation of the anaerobic process in an extended aeration system.

Some assistance could be given to design a new ETP, with some possibility of reuse of the existing equipment. This assistance could concern only the control of the project made by an engineering company. It must be noted that already, the chrome floats are precipitated and the sludge is sent to another factory for recovery.

The tannery was deeply modernised and many of the old pits were delete. Today the factory looks very clean and storage of chemicals is organised in very good conditions.

5.4. Melvisharam CETP

In order to evaluate the possibility to operate a CETP in good controlled conditions, a control panel was installed at Melvisharam CETP. The control panel is functioning well and the automatic control of the plant led to a power saving of 5.5 % of energy. It has also the consequence to reduce the people employed in the CETP from 41 to 17. These people were given other jobs in other CETP.

The only pending problem is concerning the pH measurement. It is absolutely necessary that the quantity of the lime added be controlled with the pH probe. The cleaning system of the electrode must be improved. In any case, it is necessary to operate a manual cleaning every week with pH probes in tannery effluents.

5.5. PKL ETP

PKL tested bacteria in the biological stage of the ETP. The aim of the experiment was to improve the reduction in COD as the chemical manufacturer is claiming that a level as low as 100 mg/l can be achieved. Trials were started at the beginning of the month but were stopped because of the rain that diluted too much the influent. A new experiment is pending and will be extended on several months. During the first 15 days, a bacteria concentration of 100 mg/l is sent to biological treatment. For the following 15 days, the dosage is reduced to 50 mg/l, then 10 mg/l and 5 mg/l. After

two months, the normal delivery will be limited to 2-5 mg/l. For the first month, the cost of chemicals is estimated to 30000 Rs (for 200 m³/d).

6. Cleaner technologies

6.1. Proposal for introduction of recycling of lime liquor, pelt wash liquor in K. R. Leathers, Ranipet.

Mr Viswanathan prepared a document on progress on recycling of lime liquor in K.R. Leathers. To improve the results already obtained, the following recommendations should be followed:

- The calculation of the sulphide is done with pure sulphide and does not take into account the concentration of sulphide in commercial product (about 25 %). For example, the trial N° 9 with a concentration of 1.24 mg/l of S⁻ is equivalent to 5 g/l of commercial Na₂S. This means that 2000 litres of liquor contains 10 kg of Na₂S and the reduction in chemicals is 25 %. This value is a good value for a process with painting, where the oxidation of sulphide can take place more easily than in a normal float process.
- The quantity of water to be added in the float should be minimised to prevent too much dilution of the float. In normal conditions, with elimination of skins from the paddle and with sedimentation of the float after pumping, 70 % of the volume can be recovered and this could lead to a good recovery rate.
- In trials N°2 and 3, Somalia goatskins are used for the recycling process. In trial N°4, some raw hide are processed. It is difficult to compare these two types of product that should give different results. If possible, it should be better to test the recycling operation with one type of product, hides, goatskins or sheepskins.
- Nitrogen is an interesting parameter for the test, in order to evaluate the increase in dissolved proteins and the risk to limit the swelling of hides or skins. Nitrogen could be analysed in the first float and in the following recycled float. It could be analysed also after 8 or 9 recycling cycles in order to evaluate its increase.
- There is no need to analyse BOD₅ that could give erratic results in the presence of sulphide.
- The sulphide measure must be done after a correct sampling (no air in the closed bottle) and after a very short period, not exceeding 24 hours. It should be better to operate the test inside the tannery with a low accuracy but simple method such as the zinc sulphate method. This method is used to control the sodium sulphide quality and is annexed.

During a visit on site the main points raised above were discussed with Mr Jagan. It was possible to see the equipment used for the recycling and to confirm the solutions to improve the situation. The first tannery selected was not confirmed

because of the use of enzymatic products and another tannery, KR Leathers located close to PRC was selected.

6.2 Other cleaner technologies to be tested

Besides partial salt recovery, liming recycling and chrome precipitation and reuse, selected cleaner processes that could be tested in tanneries are: enzymatic treatment for liming, hair saving unhairing liming methods, low salt in pickling or pickling float recycling, wet white production to split and shave before tanning, direct recycling of chromium, chrome free tanning, HVLP guns in finishing and water conservation procedures.

7. Other points discussed

PDU selected for publication in Tamil language

We agreed to select 7 PDU for a large editing and translation into Tamil language. The selected subjects are: PDU 4, 5, 6, 7, 8, 12, and 16.

Poster presentation

During the mission the posters to be presented for the next IULTCS Congress in Cape Town (7 to 10 March 2001) were revised and some modifications proposed.

Videos

Three videos already prepared on TDS, sludge, and solid wastes were controlled and some modifications were discussed mainly in the TDS video.

Laboratory equipment for Bangladesh

On 7th February the offers for laboratory control equipment in Bangladesh were evaluated with KV Emmanuel and analysed. Some item considered as too expensive, such as the Buchi fully automatic equipment for nitrogen measurement cannot be considered as indispensable. With some glassware and heating equipment, already in the offer, it is possible to have the same type of testing.

Revised by Michel Aloy

23/04/2001

Annexe 1 - Analytical procedure for fast sulphide testing in tannery laboratory

Chemicals to be used

The method uses the following chemicals:

- Buffer solution: The precision of the titration method by zinc sulphate depends from the quantities of ammonium chloride and ammonia being present in the solution to be tested. This solution must contain:
 - ammonia 0.5 N
 - ammonium chloride 0.25 N.
- Solution containing 0.05 M $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ (14.35 g/l)
- Lead acetate paper (filter paper impregnated with a lead acetate solution 10 % and dried).

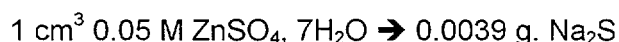
Operating procedure

Take a quantity of liquor to be tested representing about 2 g of Na_2S and dilute it with distilled water to obtain 500 ml of solution. Filter it to obtain a clear solution.

Take in a becher of 250 ml capacity, 25 ml of the buffer solution and 25 ml of the sulphide solution. Make a titration with the 0.05 M zinc sulphate solution under agitation with a glass rod until this no more soluble sulphide in the liquid.

To control the end of the titration, the glass rod is used to make some touch on the lead acetate paper, placed under a filter paper in order to prevent any contact between the zinc sulphide and the reactive paper. When there is no more brown spot in a short time, the end of filtration is checked with the filtration in a test tube of 10 cm^3 of the solution. When adding one drop of zinc sulphate solution, no more trouble can be seen. If any, the test tube content is again poured in the becher and some drops of zinc sulphate solution are added again before a new control.

Titration must be done slowly, especially at the end of the test.



Annexe 2 – PDU/9 – Irrigation with tannery effluent. Ground water analysis

Excel tables

- TDS Page 1
- Chlorides Page 2
- Sulphates Page 3
- Total hardness Page 4
- Electrical conductivity Page 5
- Balance 1999/2000 Page 6

	TDS mg/l								Mean values		Variation month/month		Proportion
	Piezometer location												
	1	2	3	4	5	6	7	8	Val 6 ft	Val 40 ft	6 ft	40 ft	40ft/6ft
janv-99	6 960	3440	4900	4080	9560	1180	6500	2700	6 980	2 850			40,8%
Feb													
Mar	7060	3100	4900	3780	8840	1300	6240	2460	6 760	2 660			39,3%
April	6593	3246	3820	4026	8906	1213	6086	2693	6 351	2 795			44,0%
May	6565	3975	4030	5380	9090	1720	6522	2725	6 552	3 450			52,7%
June	7240	3630	4375	5570	8490	1522	6850	2560	6 739	3 321			49,3%
July	7645	3315	3730	5605	8025	2045	6705	2105	6 526	3 268			50,1%
Aug	8245	3128	3973	4408	7187	1224	5620	2655	6 256	2 854			45,6%
Sept	8207	2873	3455	4253	7428	1112	4454	1772	5 886	2 503			42,5%
Oct	7568	2920	3685	5400	7005	1133	5810	2047	6 017	2 875			47,8%
Nov	7568	3184	3819	5343	7673	1761	6126	1817	6 297	3 026			48,1%
Dec	7546	3812	4020	6308	8315	1714	6498	1951	6 595	3 446			52,3%
janv-00	6781	3583	4096	4324	8744	1152	6120	1731	6 435	2 698	-8,5%	-5,7%	41,9%
Feb	6047	3769	4093	4416	9060	1663	5917	2021	6 279	2 967			47,3%
Mar	5710	3768	4028	4298	9033	1594	5803	2237	6 144	2 974	-10,0%	10,6%	48,4%
Apr	5778	3937	3918	4208	9017	1475	5798	2409	6 128	3 007	-3,6%	7,1%	49,1%
May	5986	4353	4240	4280	9253	1373	5873	2466	6 338	3 118	-3,4%	-10,6%	49,2%
June	5979	4351	3478	4995	9327	1697	5143	2643	5 982	3 422	-12,7%	3,0%	57,2%
July	6641	5009	4200	5914	7985	1722	6460	2515	6 322	3 790	-3,2%	13,8%	60,0%
Aug	6683	5182	4448	5188	8245	1779	6502	2287	6 470	3 609	3,3%	20,9%	55,8%
Sept	6433	5056	4476	4566	9113	1845	6397	1697	6 605	3 291	10,9%	24,0%	49,8%
Oct	6142	5078	4406	3784	9109	1175	6374	1368	6 508	2 851	7,5%	-0,8%	43,8%
Nov	5957	4844	4345	4125	9562	1148	6379	1485	6 561	2 901	4,0%	-4,3%	44,2%
Dec	5651	4747	4236	3814	9687	1173	6413	1569	6 497	2 826	-1,5%	-22,0%	43,5%
Mean value	6 738	3 926	4 116	4 698	8 637	1 466	6 113	2 170	6 401	3 065	-1,5%	3,7%	00/99
Maximum	8 245	5 182	4 900	6 308	9 687	2 045	6 850	2 725	6 980	3 790			
Minimum	5 651	2 873	3 455	3 780	7 005	1 112	4 454	1 368	5 886	2 503			
max variat.	2 594	2 309	1 445	2 528	2 682	933	2 396	1 357	1 094	1 288			
in %	38%	59%	35%	54%	31%	64%	39%	63%	17%	42%			

Sample collection point :

1. Near Trench	: 6 Feet	2. Near Trench	: 40 Feet
3. Ridges & Furrows	: 6 Feet	4. Ridges & Furrows	: 40 Feet
5. Park Area	: 6 Feet	6. Park Area	: 40 Feet
7. Pond Area	: 6 Feet	8. Pond Area	: 40 Feet

**PDU/9 Irrigation with tannery effluent
Ground water analysis**

Chlorides mg/l

	Piezometer location								Mean values		Variation month/month		Proportion
	1	2	3	4	5	6	7	8	Val 6 ft	Val 40 ft	6 ft	40 ft	40ft/6ft
janv-99	1340	780	549	549	1906	223	946	307	1 185	465			39,2%
Feb													
Mar	1275	680	519	662	1721	206	936	323	1 113	468			42,0%
April	1491	703	518	560	1778	212	939	370	1 182	461			39,0%
May	1949	784	583	1271	2369	332	992	324	1 473	678			46,0%
June	1364	786	653	931	1857	263	1051	433	1 231	603			49,0%
July	1826	770	768	1617	2013	252	927	435	1 384	769			55,5%
Aug	2272	814	770	1255	2404	253	966	689	1 603	753			47,0%
Sept	1846	779	770	846	1818	249	1036	526	1 368	600			43,9%
Oct	1702	717	760	1114	1886	285	1276	541	1 406	664			47,2%
Nov	1633	1030	846	1201	2262	263	1339	537	1 520	758			49,9%
Dec	1595	1034	963	1119	2692	371	1371	509	1 655	758			45,8%
janv-00	1415	1028	1056	945	2915	310	1302	501	1 672	696	29,1%	33,2%	41,6%
Feb	1215	986	1001	920	2924	395	1226	534	1 592	709			44,5%
Mar	1070	888	862	832	2536	304	1103	526	1 393	638	20,1%	26,6%	45,8%
April	1100	959	840	803	2436	335	1120	603	1 374	675	14,0%	31,7%	49,1%
May	1167	1093	887	881	2359	373	1145	613	1 390	740	-6,0%	8,4%	53,3%
June	1096	1056	830	996	2170	353	1219	542	1 329	737	7,3%	18,1%	55,4%
July	1247	1075	845	1101	1939	355	1050	606	1 270	784	-8,9%	2,0%	61,7%
Aug	1276	1097	873	920	2015	466	1171	530	1 334	753	-20,2%	0,1%	56,5%
Sept	1166	1046	865	839	2367	412	1139	499	1 384	699	1,2%	14,2%	50,5%
Oct	1058	1089	821	671	2937	250	888	282	1 426	573	1,4%	-15,9%	40,2%
Nov	1030	998	821	713	2512	329	1001	356	1 341	599	-13,3%	-26,5%	44,7%
Dec	982	961	797	680	2412	222	1099	318	1 323	545	-25,2%	-39,1%	41,2%
Mean value	1 396	920	791	932	2 271	305	1 097	474	1 389	658	2,0%	6,6%	00/99
Maximum	2 272	1 097	1 056	1 617	2 937	466	1 371	689	1 672	784			
Minimum	982	680	518	549	1 721	206	888	282	1 113	461			
max variat.	1 290	417	538	1 068	1 216	260	483	407	559	323			
in %	92%	45%	68%	115%	54%	85%	44%	86%	40%	49%			

Sample collection point :

1. Near Trench	: 6 Feet	2. Near Trench	: 40 Feet
3. Ridges & Furrows	: 6 Feet	4. Ridges & Furrows	: 40 Feet
5. Park Area	: 6 Feet	6. Park Area	: 40 Feet
7. Pond Area	: 6 Feet	8. Pond Area	: 40 Feet

Sulphates mg/l

	Piezometer location								Mean values		Variation month/month		Proportion
	1	2	3	4	5	6	7	8	Val 6 ft	Val 40 ft	6 ft	40 ft	40ft/6ft
janv-99	1028	633	1740	1050	1922	230	1806	831	1 624	686			42,2%
Feb													
Mar	1004	912	1724	981	1641	234	1816	889	1 546	754			48,8%
April	1042	733	1653	1047	1462	586	1831	828	1 497	799			53,3%
May	1168	916	1728	1071	1043	425	1837	805	1 444	804			55,7%
June	1068	989	1881	1064	1175	477	1858	724	1 496	814			54,4%
July	1025	1098	903	1014	1009	407	1733	671	1 168	798			68,3%
Aug	1120	1148	1025	1075	1157	416	1056	759	1 090	850			78,0%
Sept	1825	1202	1491	1845	1501	309	1651	806	1 617	1 041			64,3%
Oct													
Nov													
Dec													
janv-00	995	1164	1111	1024	1189	473	1036	1061	1 083	931	-50,0%	26,3%	85,9%
Feb	1176	1180	1069	1053	1183	520	1040	757	1 117	878			78,6%
Mar	1135	1121	1111	1121	1297	601	1138	839	1 170	921	-32,1%	18,1%	78,7%
April	1277	1143	1306	1238	1337	712	1173	859	1 273	988	-17,6%	19,2%	77,6%
May	1438	1282	1339	1230	1327	687	1285	925	1 347	1 031	-7,2%	22,0%	76,5%
June	1456	1205	1454	1380	1493	603	1230	913	1 408	1 025	-6,2%	20,7%	72,8%
July	1423	1242	1946	1545	1552	680	1551	1111	1 618	1 145	27,8%	30,3%	70,7%
Aug													
Sept													
Oct	1460	1484	1651	1289	1647	598	1812	600	1 643	993			60,4%
Nov	1517	1388	1721	1587	1607	624	1919	780	1 691	1 095			64,7%
Dec	1522	1467	1786	1593	1661	543	1969	654	1 735	1 064			61,4%
Mean value	1 260	1 128	1 480	1 234	1 400	507	1 541	823	1 420	923	-1,9%	18,8%	00/99
Maximum	1 825	1 484	1 946	1 845	1 922	712	1 969	1 111	1 735	1 145			
Minimum	995	633	903	981	1 009	230	1 036	600	1 083	686			
max variat.	830	851	1 043	864	913	482	933	511	652	459			
in %	66%	75%	70%	70%	65%	95%	61%	62%	46%	50%			

Sample collection point :

1. Near Trench	: 6 Feet	2. Near Trench	: 40 Feet
3. Ridges & Furrows	: 6 Feet	4. Ridges & Furrows	: 40 Feet
5. Park Area	: 6 Feet	6. Park Area	: 40 Feet
7. Pond Area	: 6 Feet	8. Pond Area	: 40 Feet

Total hardness mg/l

	Piezometer location								Mean values		Variation month/month		Proportion
	1	2	3	4	5	6	7	8	Val 6 ft	Val 40 ft	6 ft	40 ft	40ft/6ft
janv-99	700	2130	2900	2940	7400	870	1960	1400	3 240	1 835			56,6%
Mar	590	1640	2100	2800	6400	880	1812	1384	2 726	1 676			61,5%
April	754	1683	2136	2643	7466	883	1696	1276	3 013	1 621			53,8%
May	950	1605	2052	2700	6800	877	1675	1012	2 869	1 549			54,0%
June	1025	1702	2435	2025	6925	910	1740	1187	3 031	1 456			48,0%
July	1425	1715	1935	1825	6650	950	1332	1267	2 836	1 439			50,8%
Aug	1930	1730	2123	2360	3803	933	1200	1326	2 264	1 587			70,1%
Sept	1446	1780	2070	1796	2773	983	1713	1346	2 001	1 476			73,8%
Oct	1706	1773	2183	2340	3290	953	2036	1206	2 304	1 568			68,1%
Nov	1360	2203	2323	2476	3120	803	1933	1300	2 184	1 696			77,6%
Dec	1160	2822	2662	2260	3362	929	1842	1395	2 257	1 852			82,1%
janv-00	1083	2900	2560	1866	3303	1036	2013	1296	2 240	1 775	-44,7%	-3,4%	79,2%
Feb	1056	2700	2520	1550	3073	856	1556	1076	2 051	1 546			75,3%
Mar	957	2560	2270	1432	2715	917	1585	1282	1 882	1 548	-44,8%	-8,3%	82,3%
April	1643	2870	3293	2023	3310	1186	2293	2440	2 635	2 130	-14,4%	23,9%	80,8%
May	1350	2663	2220	1811	3343	966	2260	1746	2 293	1 797	-25,1%	13,8%	78,3%
June	1371	2894	2080	1816	2904	930	1990	1560	2 086	1 800	-45,3%	19,1%	86,3%
July	1350	2897	2220	1812	2905	975	1900	1685	2 094	1 842	-35,4%	21,9%	88,0%
Aug	1525	2967	2272	1545	2992	1095	1872	1632	2 165	1 810	-4,6%	12,3%	83,6%
Sept	1462	2675	2242	1262	3265	1025	1777	1237	2 187	1 550	8,5%	4,7%	70,9%
Oct	1165	2610	2015	880	3600	765	1557	885	2 084	1 285	-10,5%	-22,0%	61,7%
Nov	1127	2792	1960	1075	3655	767	1657	1095	2 100	1 432	-4,0%	-18,4%	68,2%
Dec	1164	2854	1974	1012	3336	938	1598	1002	2 018	1 452	-11,8%	-27,6%	71,9%
Mean value	1 230	2 355	2 285	1 924	4 191	932	1 782	1 349	2 372	1 640	-21,3%	3,0%	00/99
Maximum	1 930	2 967	3 293	2 940	7 466	1 186	2 293	2 440	3 240	2 130			
Minimum	590	1 605	1 935	880	2 715	765	1 200	885	1 882	1 285			
max variat.	1 340	1 362	1 358	2 060	4 751	421	1 093	1 555	1 358	845			
in %	109%	58%	59%	107%	113%	45%	61%	115%	57%	52%			

Sample collection point :

1. Near Trench	: 6 Feet	2. Near Trench	: 40 Feet
3. Ridges & Furrows	: 6 Feet	4. Ridges & Furrows	: 40 Feet
5. Park Area	: 6 Feet	6. Park Area	: 40 Feet
7. Pond Area	: 6 Feet	8. Pond Area	: 40 Feet

EC mmhos/cm

	Piezometer location								Mean values		variation month/month		Proportion
	1	2	3	4	5	6	7	8	Val 6 ft	Val 40 ft	6 ft	40 ft	40ft/6ft
janv-99	10,7	5,3	7,5	6,3	14,7	1,8	10,0	4,2	10,7	4,4			40,8%
Mar	10,9	4,8	7,5	5,8	13,6	2,0	9,6	3,8	10,4	4,1			39,3%
April	10,1	5,0	5,9	6,2	13,7	1,9	9,4	4,1	9,8	4,3			44,0%
May	10,1	6,1	6,2	8,3	14,0	2,6	10,0	4,2	10,1	5,3			52,7%
June	11,1	5,6	6,7	8,6	13,1	2,3	10,5	3,9	10,4	5,1			49,3%
July	11,8	5,1	5,7	8,6	12,3	3,1	10,3	3,2	10,0	5,0			50,1%
Aug	12,7	4,8	6,1	6,8	11,1	1,9	8,6	4,1	9,6	4,4			45,6%
Sept	12,6	4,4	5,3	6,5	11,4	1,7	6,9	2,7	9,1	3,9			42,5%
Oct	11,6	4,5	5,7	8,3	10,8	1,7	8,9	3,1	9,3	4,4			47,8%
Nov	11,6	4,9	5,9	8,2	11,8	2,7	9,4	2,8	9,7	4,7			48,1%
Dec	11,6	5,9	6,2	9,7	12,8	2,6	10,0	3,0	10,1	5,3			52,3%
janv-00	10,4	5,5	6,3	6,7	13,5	1,8	9,4	2,7	9,9	4,2	-8,5%	-5,7%	41,9%
Feb	9,3	5,8	6,3	6,8	13,9	2,6	9,1	3,1	9,7	4,6			47,3%
Mar	8,8	5,8	6,2	6,6	13,9	2,5	8,9	3,4	9,5	4,6	-10,0%	10,6%	48,4%
Apr	8,9	6,1	6,0	6,5	13,9	2,3	8,9	3,7	9,4	4,6	-3,6%	7,1%	49,1%
May	9,2	6,7	6,5	6,6	14,2	2,1	9,0	3,8	9,8	4,8	-3,4%	-10,6%	49,2%
June	9,2	6,7	5,4	7,7	14,3	2,6	7,9	4,1	9,2	5,3	-12,7%	3,0%	57,2%
July	10,2	7,7	6,5	9,1	12,3	2,6	9,9	3,9	9,7	5,8	-3,2%	13,8%	60,0%
Aug	10,3	8,0	6,8	8,0	12,7	2,7	10,0	3,5	10,0	5,6	3,3%	20,9%	55,8%
Sept	9,9	7,8	6,9	7,0	14,0	2,8	9,8	2,6	10,2	5,1	10,9%	24,0%	49,8%
Oct	9,4	7,8	6,8	5,8	14,0	1,8	9,8	2,1	10,0	4,4	7,5%	-0,8%	43,8%
Nov	9,2	7,5	6,7	6,3	14,7	1,8	9,8	2,3	10,1	4,5	4,0%	-4,3%	44,2%
Dec	8,7	7,3	6,5	5,9	14,9	1,8	9,9	2,4	10,0	4,3	-1,5%	-22,0%	43,5%
Mean value	10,4	6,0	6,3	7,2	13,3	2,3	9,4	3,3	9,8	4,7	-1,5%	3,7%	00/99
Maximum	12,7	8,0	7,5	9,7	14,9	3,1	10,5	4,2	10,7	5,8			
Minimum	8,7	4,4	5,3	5,8	10,8	1,7	6,9	2,1	9,1	3,9			
max variat.	4,0	3,6	2,2	3,9	4,1	1,4	3,7	2,1	1,7	2,0			
in %	38%	59%	35%	54%	31%	64%	39%	63%	17%	42%			

Sample collection point :

1. Near Trench : 6 Feet	2. Near Trench : 40 Feet
3. Ridges & Furrows : 6 Feet	4. Ridges & Furrows : 40 Feet
5. Park Area : 6 Feet	6. Park Area : 40 Feet
7. Pond Area : 6 Feet	8. Pond Area : 40 Feet

Mean values of analytical parameters

