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Studio Tecnico

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Florence (Italy)

Project US/BRA/80/166

Contract 85/48/MK

United Nations Industrial Development Organization

U.N.I.D.O.

Vienna International Centre

ASSISTANCE IN THE ESTABLISHMENT AND OPERATION OF A PILOT AND DEMONSTRATION PLANT FOR TANNERY EFFLUENTS TREATMENT AT ESTANCIA VELHA - R.S. - BRAZIL

SECOND PHASE

Final Report

Notice:

Based on work of Messrs. G. Clonfero, P. Nini, G. Franci, M. Bacchi

March 1987

English

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SUMMARY

This report contains a description of the most significant activity undertaken in accordance with UNIDO Contract N° 85/48/MK carried out during a nine months' period from July '85 to December '86. Our Team worked in close collaboration with Mr. David WINTERS (*), UNIDO Chief Technical Adviser, and with the Serviçio Nacional de Aprendizagem Industrial (SENAI) R.S., as Counterpart.

The activity and the results of the first phase of the Project are described in our Final Report, dated July 1984, and are briefly summarized in paragraph 1 of this paper together with the causes that have induced UNIDO to extend the Project and the Republic of Italy to provide the necessary funds.

The first phase was characterized by the following activities:

- experimental tests in the pilot plant at Estancia Velha R.S. and demonstration, under local conditions, of the effectiveness of the different treatment units and equipment ;
- training in tannery wastes treatment of the Brazilian personnel of the Project and other technicians belonging to State Environmental Institutes, Tanneries and Consulting-Engineering Companies;
- dissemination of tannery effluents treatment techniques and pilot plant results;
- assistance, generally consisting in design and modification of primary treatments, to tanneries principally located in Rio Grande do Sul.

The second phase, to which this report is related, has been characterized by:

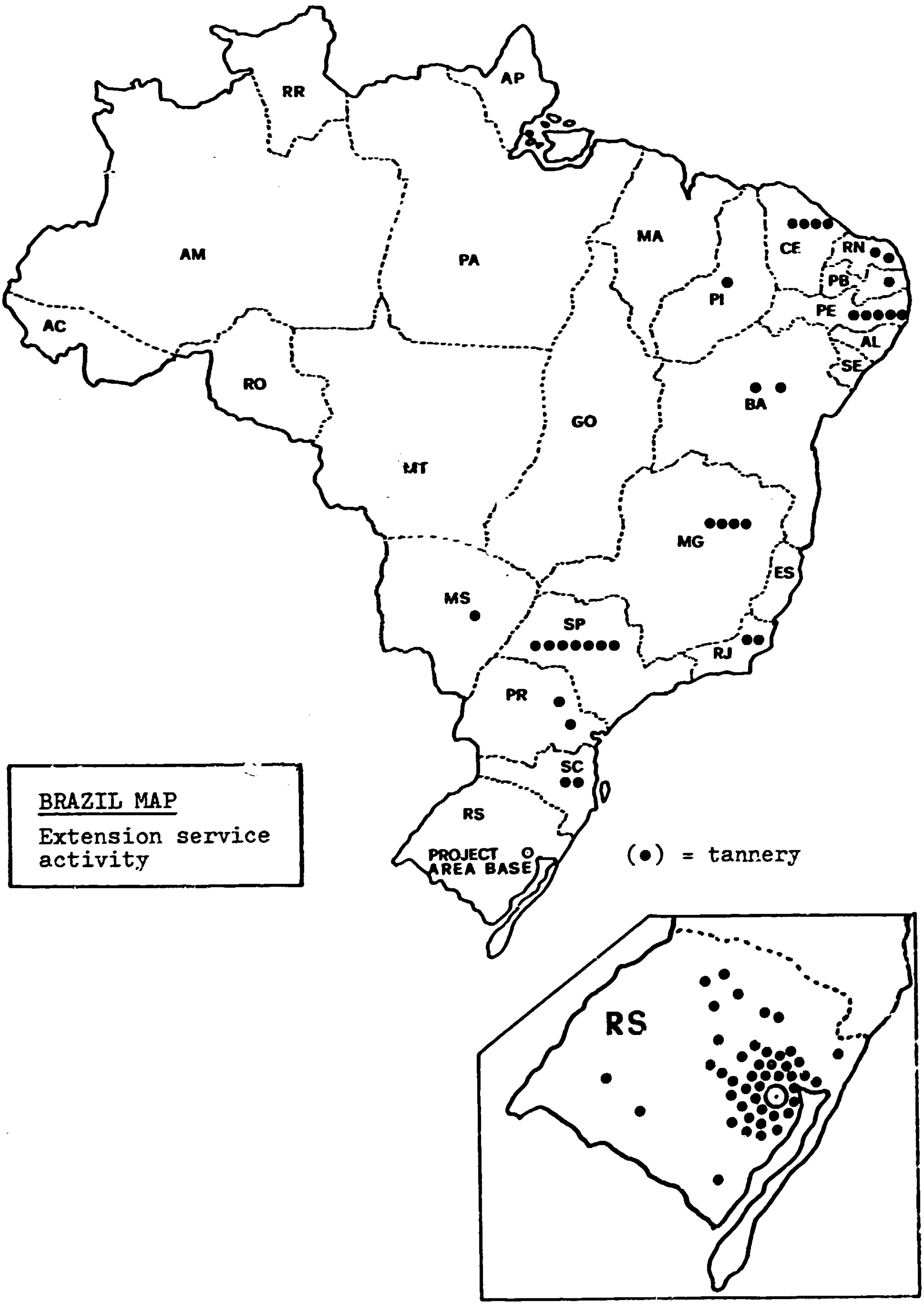
- a massive demand for technical assistance in effluents treatment projects from tanneries located throughout in

Brazil ;

- an increase of the extension also to secondary treatment projects;
- a more active participation of the Brazilian Project Team in preparation of projects: the activity of the foreign experts was limited to designing outlines and "cleaning" the prepared projects;
- a limitation of the Project Staff activity in the pilot plant to day by day survey of a plant that operated more for demonstration than for experiments; training activity was limited to the new units (ultrafiltration and flotation tests;
- a series of theoretical-practical courses probing secondary treatments and solid waste disposal in tanning.

The predominant activity of this second phase was clearly the assistance to Brazilian tanneries. The results were superior to expectations as to create some difficulties: the tanneries' requests for assistance have almost oustripped the availability of Project Personnel.
The Brazil map reproduced on pag. 3 illustrates the tanneries for which the Project has furnished technical assistance and gives an idea of the quantity of work accomplished. More than one hundred factories were visited and investigated, and close to 7[illegible] outlines of effluents-treatment projects or project modifications prepared. Near 30 of these outlines have since been drawn in detail by the Brazilian Team, and about 10 are in course of preparation.

(*) During the preparation of this report we learned of the untimely death of Mr. David WINTERS whose guidance in this work was paramount to the Project's success.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PROJECT
AREA BASE
BRAZIL MAP
Extension service
activity
(•) = tannery
RS

1. BACKGROUND INFORMATION AND CONTRACTUAL DUTIES

1.1 Background information

The original Project drawn up in 1979 was formalized in October 1981. It come to an end in March 1985, when the donor's (the Republic of Italy) funds were used up.
At the time it was recognized that, despite some initial difficulties, the Project had achieved its main goals:

- the installation of a pilot demonstrative plant for tannery effluents at Estancia Velha where a relevant part of the Brazilian tannery industry is located and a SENAI Schoool which trains tannery technicians from throughout Latin America exists. This pilot plant, unique in the leather sector, is capable of treating up to 100 m^3/day of tannery effluents and includes a primary treatment system, four parallel alternative biologic treatment units and two sludge dewatering systems. The plant facilities also include environmental processes such as chrome recovery and lime baths recycling. Many of the conventional treatments were tested and evaluated under local conditions. It was shown that all the system adopted in the pilot plant, under correct design and operating parameters, can reduce the level of tannery pollutants and so are to be recommended to tanners. The Project's philosophy was never to impose on Brazil treatments used in Europe or in other developed countries, but to offer the industrialists and the local authorities a wide choice of alternatives tested under local conditions.
- The laboratory and the equipment of the School were amplified in order that all relevant effluents and solid wastes might be analysed.
- The Project Personnel served effectively as liasor between

local authorities (especially in R.S.) and tanners.

- The Project became a centre of knowledge and expertise which could offer technical services to the tannery industry in Brazil and the entire Latin American region and could train personnel to introduce better environmental processes, treatment and control of tannery wastes.
- The SENAI Team (8 persons), fully trained in tannery effluents treatment, was available for extension and dissemination services.
- A large number of tanneries were visited by the Project Staff, who prepared detailed modification and/or implementation projects.
- Efforts had been spent in spreading pilot plant results. This activity was crowned by an "open week" at Estancia Velha in March 1984. About 130 participants (tannery industrialists and technicians, environmental authorities, consulting engineers) attended the meeting and heard over 20 lectures on tannery effluents and solid wastes treatment.

However, in order that the local tannery industry reap benefit from these results, the Project's activity in the extension service area must continue. The original Project had been designed in accordance with sectorial requirements (1979 D.M.A. regulations for waste water discharge in the State of R.S.) and subsequently other Brazilian States had prepared their own regulations.

Under such circumstances the need was felt for further activities principally in those States where a significant number of tanneries exists. Furthermore, the tanners'delay of implementation of primary treatment plants limited the activity in the secondary treatments (a secondary treatment cannot be dimensioned or installed without a reasonably operative primary one).

Since it was evident that the Brazilian Staff would soon be subjected to a vast amount of work and responsability the assistance and the presence in field of foreign experts for an additional minimal period of 9 months would be required.

For these reasons UNIDO decided an extension (2nd phase) of the original Project, and the necessary funds were again provided by the Italian Government.

The Studio Tecnico Dr. Giuseppe CLONFERO, Florence, whose expertise in tannery effluents treatment had a relevant part in the success of the first phase of the Project, was sub-contracted by UNIDO on 5 June 1985 to provide the technical assistance and support to this second phase.

1.2 Contractual duties

The contractual duties are reported in term of reference in Annex I.

The Expert Team provided 10.5 man/month work (9m/m in field and 1.5 m/m at home base) spread over 17 months ca.

The personnel assigned to the Project were as follow:

- Mr. Giuseppe CLONFERO Chemist (Team Leader)
- Mr. Piero NINI "
- Mr. Giovanni FRANCI Geologist
- Mr. Manuele BACCHI Biologist

Reports

The Studio has submitted to UNIDO, before this Final Report, the reports listed below:

- Flash Report July 1985;
- First Progress Report March 1986;

- Second Progress Report June 1986;
- Third Progress Report July 1986;
- Draft Final Report January 1987.

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2. PILOT PLANT

2.1 Pilot plant

During this second phase, the pilot plant was fully operative even if more for training and demonstration than for new experiments. The layout of the pilot plant is shown in fig. 1; for the characteristics of the equipment installed and treatment units see our first phase Final Report dated July '84. The treatment stations used during this period were the following:

Stations	Utilization
- primary treatment	continuous
- secondary treatment:	
. oxidation ditch	continuous
. conventional activated sludge	continuous
. areated lagoon	concinuous
- sludge treatment:	
. thickening and filter press	periodically for demonstrative tests
. sand drying beds	continuous
- chrome recovery from spent tanning baths and sulphide removal and proteins precipitation from spent unhairing baths	periodically for demonstrative tests
- ultrafiltration and flotation units	periodically for test activity and/or demonstrative and training purposes

The pilot plant's everyday activities were controlled and monitored by all members of Brazilian Staff on rotation. The main operative performances of the various station and the mean analytical results are reported in the following tables.

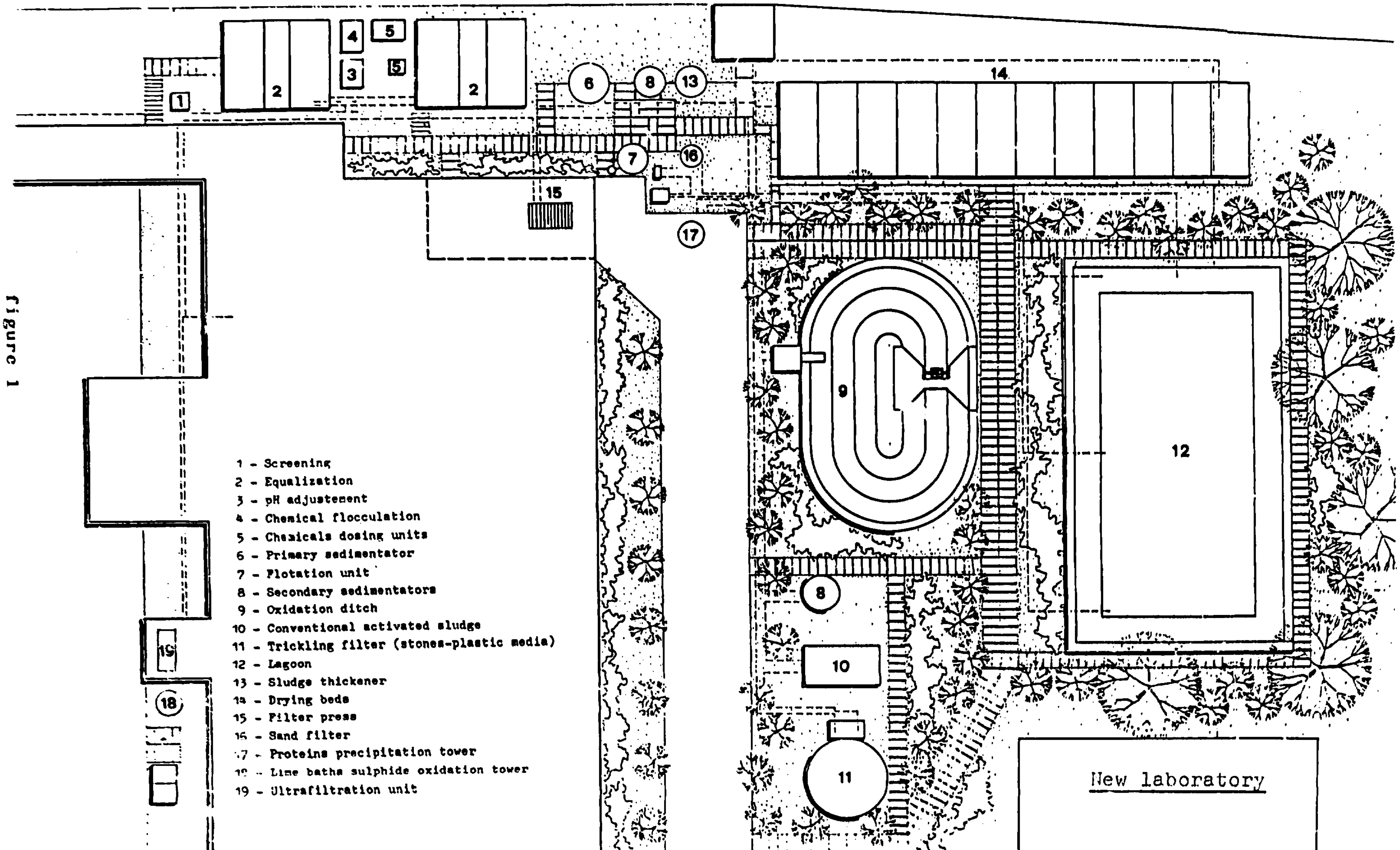
1 - Screening
2 - Equalization
3 - pH adjustement
4 - Chemical flocculation
5 - Chemicals dosing units
6 - Primary sedimentator
7 - Flotation unit
8 - Secondary sedimentators
9 - Oxidation ditch
10 - Conventional activated sludge
11 - Trickling filter (stones-plastic media)
12 - Lagoon
13 - Sludge thickener
14 - Drying beds
15 - Filter press
16 - Sand filter
17 - Proteins precipitation tower
18 - Lime baths sulphide oxidation tower
19 - Ultrafiltration unit
New laboratory

figure 1

OPERATIONAL PERFORMANCES OF THE PILOT PLANT

a) Daily volume of waste water pumped from the external tannery and treated in the pilot plant: 90 ÷ 105 m^3/day

- feeding pump capacity = 13 m^3/h
- pumping time = 7 ÷ 8 h /day

b) Primary treatment

- screening: (brushed self-cleaning type)
  . holes = Ø 1.6 mm
  . flow = 13 m^3/h
- homogeneization and sulphide oxidation:
  two tanks each of 50 m^3 (two rotary blowers and diffusers):
  . total air supplied = 300 Nm^3/h
  . total installed power = 6 kW
  . specific power = 60 W/m^3 ca
  . quantity of catalyst ($MnSO_4$) added = 20 mg/l , i.e. 2 kg/day as Mn^{++}
  . mean retention time = 25 h
- lifting pump:
  . flow = 4 ÷ 5 m^3/h
  . pumping time = 20 ÷ 24 h /day
- pH control unit: no adding of chemicals
- flocculation:
  . one 1,000 litres tank
  . stirring device = 0.7 kW
  . retention time = 10 ÷ 15 min
- Aluminium Sulphate dosing unit:
  . one 1,000 litres tank
  . stirring device = 0.7 kW
  . dosing pump = 0.2 kW
  . dosed quantity = 200 ÷ 300 mg/l , i.e. 20 ÷ 30 kg/day of commercial product
- Polyelectrolyte dosing unit:
  . one 200 litres tank
  . stirring device = 0.37 kW
  . dosing pump = 0.2 kW
  . dosed quantity = 0.5 ÷ 1 mg/l , i.e. 50 ÷ 100 gr/day (anionic powder)
- primary sedimentation:
  . one vertical sedimentation tank = Ø 2 m ca. (cone 60°) , volume = 8 m^3, retention time = 1.6 ÷ 2 h
  . sludges removal pump (helicoidal pump) : flow = 6 m^3/h , power = 0.55 kW .

c) Secondary treatments

1. Oxidation ditch

. influent flow = 1.5 ÷ 2 m^3/h (24 h/day)

. tank volume = 60 m^3 ca

. retention time = 30 ÷ 40 h

. organic loading = 25 ÷ 30 kg BOD_5/day ca

. volumetric loading = 0.4 ÷ 0.5 kg BOD_5/m^3 per day

. F/M ratio = 0.10 ÷ 0.14 kg BOD_5/kg MLSS per day

. rotor oxygen transfer capacity = 2.2 kg O_2/h

. MLSS = 3,500 mg/l ca

. OD = 2 ÷ 4 mg O_2/l ca

. total installed power = 2.2 kW

- secondary sedimentation (oxidation ditch):

  . vertical sedimentation tank: Ø 1.36 m , volume = 4.2 m^3 ,
    retention time = 2.1 ÷ 2.8 h

2. Conventional activated sludge

. influent flow = 1 m^3/h (24 h/day)

. tank volume = 19 m^3

. retention time = 19 h

. organic loading = 15 ÷ 17 kg BOD_5/day

. volumetric loading = 0.7 ÷ 0.9 kg BOD_5/m^3 per day

. F/M ratio = 0.24 ÷ 0.28 kg BOD_5/ kg MLSS per day

. MLSS = 3,200 mg/l ca

. blower with diffusers: air flow = 80 Nm^3/h

. max.oxygen transfer capacity = 2.0 kg O_2/h (10% of efficiency adopted)

. OD = 0.2 ÷ 2.2 mg O_2/l ca

. total installed power = 3.0 kW

- secondary sedimentation (conventional activated sludge)

  . vertical sedimentation tank: Ø 1.2 m , volume = 3.2 m^3
    retention time = 3.2 h

3. Aerated lagoon

. influent flow = 1 m^3/h (24 h/day)

. tank volume = 215 m^3

. retention time = 9 days ca

. organic loading = 15 ÷ 17 kg BOD_5/day

. volumetric loading = 0.07 ÷ 0.08 kg BOD_5/m^3 per day

. specific installed power (floating aerator) = 3.5 W/m^3

PILOT PLANT: laboratory analysis (average data)

July / August 1985	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	8.0	7.9	7.7	7.8	7.2
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)					
Chloride, mg/l	3,826	4,109	3,479	3,621	3,946
Suspended Solids, mg/l		320	951	750	
Settleable Solids, ml/l	108	4.2	43	0.6	0.2
C.O.D., mg/l	4,581	2,562	763	449	1,422
B.O.D., mg/l	2,425	1,008	97	91	315

September / October 1985	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	8.0	7.6	7.6	7.7	7.5
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)	42.60	5.05	0.75	0.50	
Chloride, mg/l	3,227	3,251	3,974	3,904	3,250
Suspended Solids, mg/l	2,753	535	264	234	78
Settleable Solids, ml/l	137	9.8	3.6	6.3	1.0
C.O.D., mg/l	5,342	1,267	453	411	515
B.O.D., mg/l	1,938	753	78	39	154

November / December 1985	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	7.8	7.5	7.8	7.3	7.4
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)	11.8	1.57	0.14	0.72	0.72
Chloride, mg/l	3,721	3,871	3,547	3,611	4,001
Suspended Solids, mg/l	2,053	380	548	290	300
Settleable Solids, ml/l	83	1.3	2.6	2.1	2.4
C.O.D., mg/l	3,828	1,617	541	360	452
B.O.D., mg/l	2,137	747	100	29	102

January February 1986	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	7.7	7.8	6.2	7.1	7.7
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)	1.88	0.88	4.37	0.53	
Chloride, mg/l	3,660	3,423	3,408	2,753	3,458
Suspended Solids, mg/l	2,104	516.5		90	
Settleable Solids, ml/l	46	0.6	0.4	2	3.3
C.O.D., mg/l	2,614	1,589	745	621	794
B.O.D., mg/l	910	603	27.7	21.8	165

March April 1986	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	8.2	7.7	7.4	7.1	7.5
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)	8.6			1.02	
Chloride, mg/l	2,209	3,282	3,044	2,961	3,540
Suspended Solids, mg/l		600	750	342	
Settleable Solids, ml/l	100	3.7	1.2	7.8	2.9
C.O.D., mg/l	3,027	1,306	485	331	495
B.O.D., mg/l	1,281	703	19	131	255

May June 1986	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	8.3	8.0	8.0	7.3	7.6
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)					
Chloride, mg/l	3,843	3,518	2,357	2,166	2,060
Suspended Solids, mg/l		550	336		242
Settleable Solids, ml/l	100	13.4	2.6	1.5	1.9
C.O.D., mg/l	4,118	1,609	290	343	571
B.O.D., mg/l	1,314	654	60	94	343

July / August 1986	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	8.2	8.5	7.9	7.8	7.7
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	ABSENT
Chromium, mg/l (CrIII)	24.80	2.73	0.80	0.70	0.60
Chloride, mg/l	4,146	3,572	2,977	3,345	4,078
Suspended Solids, mg/l	2,700	735	161	160	329
Settleable Solids, ml/l	146	4.8	0.8	3.2	1.9
C.O.D., mg/l	4,178	1,965	490	286	673
B.O.D., mg/l	2,029	861	60	45	199

September / October 1986	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	7.9	7.5	7.1	6.9	
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	
Chromium, mg/l (CrIII)					
Chloride, mg/l	4,306	4,478	4,834	4,833	
Suspended Solids, mg/l	3,400	660	280	140	
Settleable Solids, ml/l	43	0.75	ABSENT	ABSENT	
C.O.D., mg/l	4,155	1,170	890	535	
B.O.D., mg/l	1,590	680	207	160	

November / December 1986	Equalization tank effluent	Primary treatment effluent	Lagoon effluent	Oxidation ditch effluent	Conventional activated sludge effluent
pH	8.0	7.2	6.9	7.1	
Sulphide, mg/l	TRACES	ABSENT	ABSENT	ABSENT	
Chromium, mg/l (CrIII)		0.64			
Chloride, mg/l	3,630	3,727			
Suspended Solids, mg/l	2,670	623	780	350	
Settleable Solids, ml/l	85	ABSENT	ABSENT	0.6	
C.O.D., mg/l	3,823	1,066	461	495	
B.O.D., mg/l	2,[illegible]	320	65	130	

2.2 Pilot plant new facilities

In this second phase the pilot plant was endowed with two new facilities: the ultrafiltration and the flotation units. The choice, made by the UNIDO C.T.A., of these processes to complete the demonstrative and experimental possibilities of the pilot plant was, in our opinion, fully justified.

Even if these techniques appear rather sophisticated for the tanning industry, they represent neverthless two treatment alternatives which a demonstrative plant, especially one located in a tannery school, must have.

Before starting practical tests, it was deemed necessary to give some lessons on the theoretical aspects of ultrafiltration and flotation. Short summaries of the treated topics are reported in Annexes II and III.

2.2.1 Ultrafiltration tests: spent unhairing baths recycle

Plant description

a. Ultrafiltration unit (see fig. 2)

The ultrafiltration unit is constituted by:

- n. 16 (8+8) tubular membranes;
- n. 1 centrifugal pump: flow 16 m^3/h, max. working pressure 4 bars;
- n. 1 holding tank with level control (capacity 100 l);
- n. 1 temperature control;
- n. 2 manometers (inlet and outlet pressure);
- n. 1 permeate flow meter.

The unit can work with 16 tubes (filtering surface 1.6 m^2) or 8 tubes (filtering surface 0.8 m^2) by means of a series of valves.

The membranes (Abcor type HFM 251 FEO) are arranged in tubular modules; this arrangement has given the best results in the treatment of spent unhairing baths and in general of waters with high content of suspended solids. A cut-away view of a tubular module is presented in fig. 3.

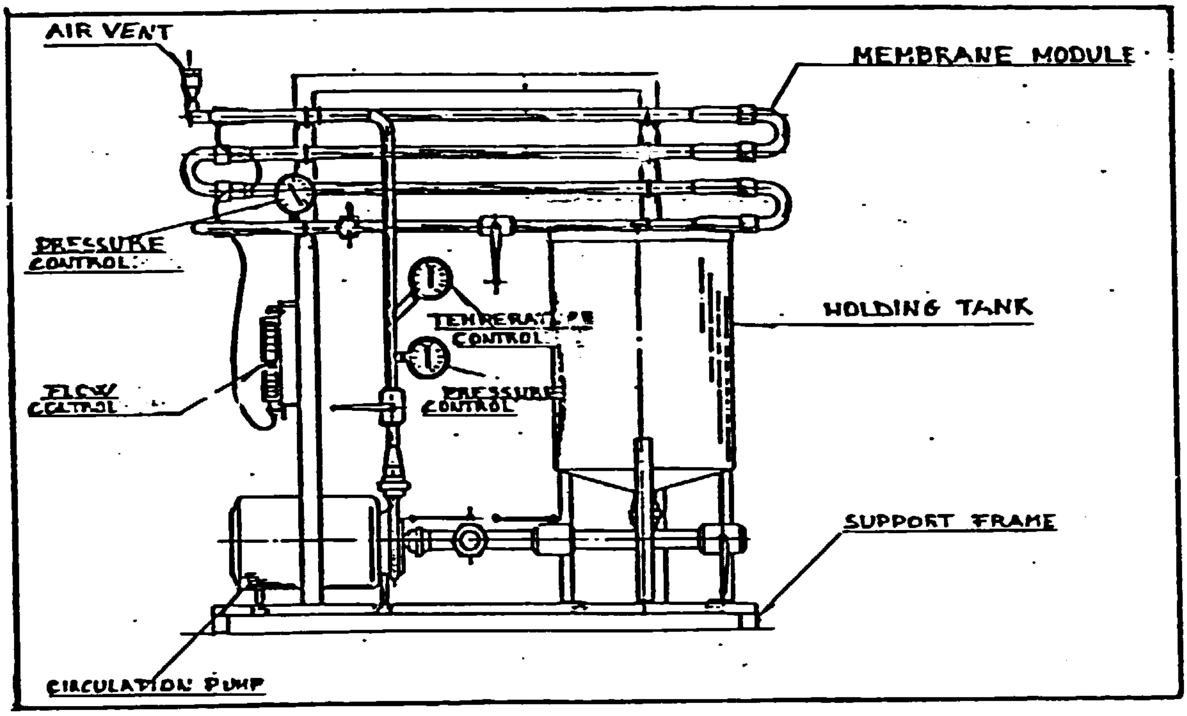

FIGURE 2

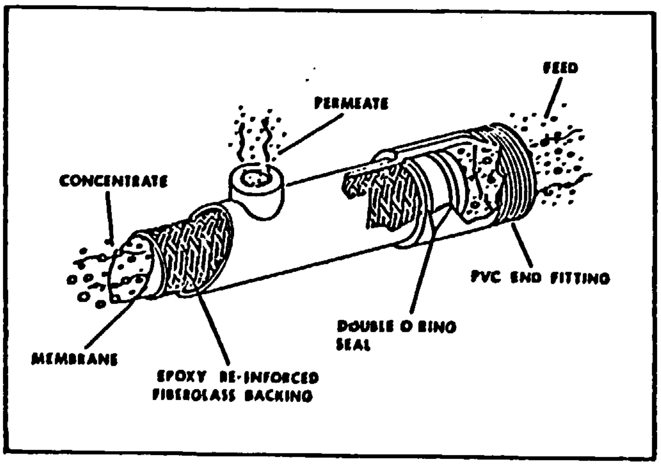

FIGURE 3

Each tube, 1.5 m long, has a membrane surface of 0.1 m^2. In table I are reported the characteristics of membrane Abcor type HFM 251 FEO.

table I

Internal diameter:	2.54 cm (1 inch)
Nominal cut off:	M.w. 18,000
Clean water flux:	100 l/m^2h at 1.5 bars and 25°C up to 1,000 l/m^2h at 3.5 bars and 25°C
Working pressure:	3.5 bars (max 10 bars)
pH range:	1 - 13
Max. working temperature	90 °C

b. Other plant facilities

- screen: self cleaning screen (Hydrasieve type) wedge wire openings 1 mm;
- holding tank: diameter 0.95 m, height 3 m, capacity 2 m^3;
- lifting pump: screw pump (Mohno type), flow 2 m^3/h.

Treatment cycle (see fig. 4)

The spent unhairing baths coming from the School are screened and collected in the holding and settling tank and, after solids sedimentation, the surnatant is pumped in the holding tank of the U.F. unit where it is mantained at a constant level by means of a level control. A centrifugal pump feeds the U.F. modules and the concentrate returns continuously to the holding tank. An heat exchanger, working with running water, has been

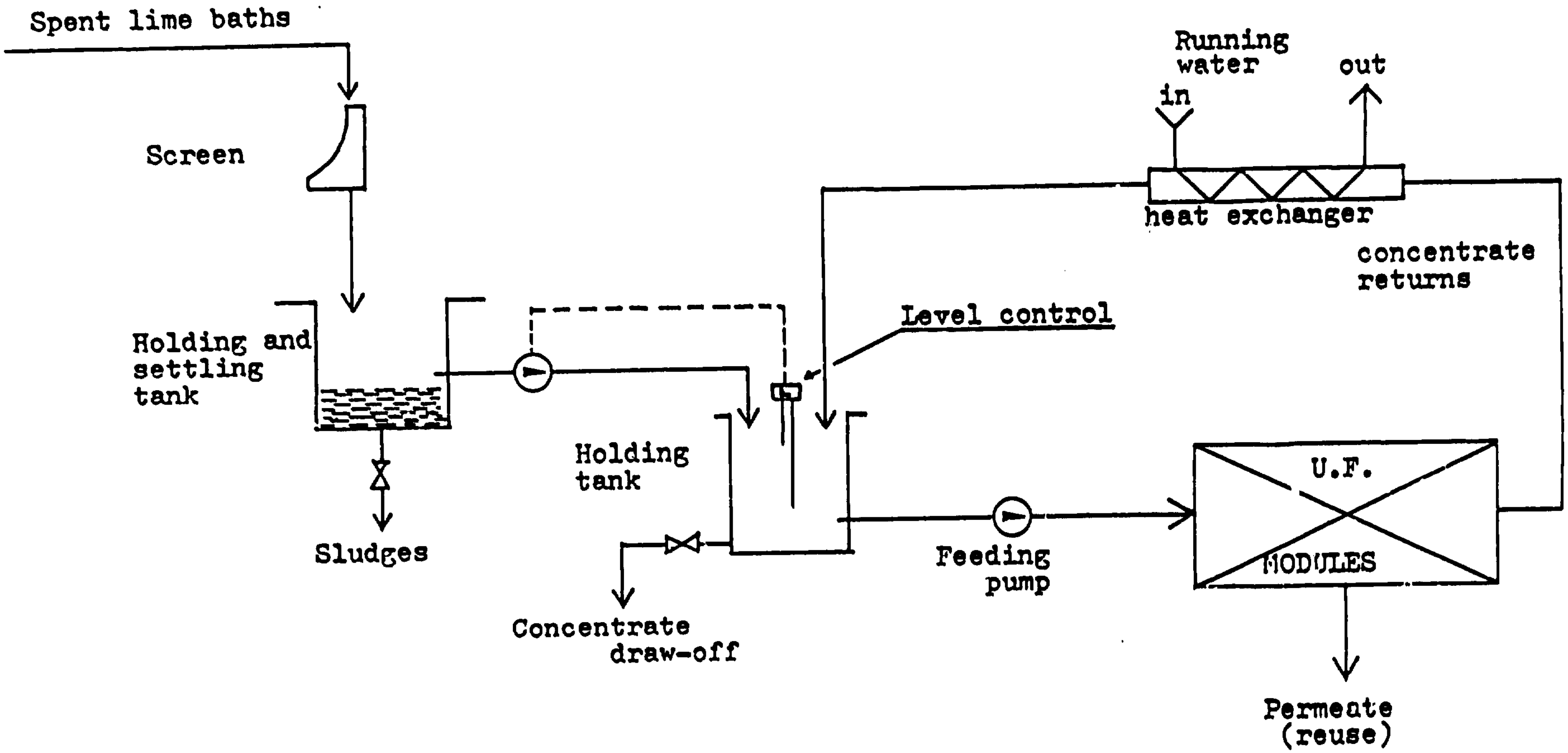
Spent lime baths
Screen
Holding and settling tank
Sludges
Holding tank
Concentrate draw-off
Level control
Running water
in
out
heat exchanger
concentrate returns
U.F.
MODULES
Feeding pump
Permeate (reuse)

figure 4

inserted on the return pipe in order to avoid excessive heating of the bath.
The permeate is continuously stored into a separate tank from which it is drawn for the analytical controls and the subsequent reuse. At the end of a processing cycle (generally one day) the content of the process tank would be concentrated to the minimum volume and discharged for further treatments.
The membrane modules are flushed daily with water and a weekly detergent cleaning is given.

Operational performances of the tests

The fresh lime bath employed by the School, was prepared in the following way:

- material processed: wet salted hides, 22-25 kg each;
- unhairing bath: 200 % water
  4 % $Ca(OH)_2$
  3 % Na_2S (52 %)
- rinsing baths: 300 % water.

The unhairing and the rinsing baths were collected and ultrafiltrated, the permeate was returned to the School for reuse. During these tests the recycle was effected with a 100 % of processed liquor (permeate) reintegrating the lime (4 % $Ca(OH)_2$ on hides weight) and the lost sulphide.

Test results

The results obtained are reported in tables II and III (hydraulic data) and IV (analytical data).
In comparison with Abcor's data, which point out a membrane flow (at standard conditions) of spent unhairing baths of 60-70 l/m^2h and with the values that we obtained in an industrial plant in Italy, 80-100 l/m^2h, the values obtained in

the first series of tests, 35-40 l/m^2h are rather low. These results can be attributed, in our opinion, to the following causes:

- lack of pre-sedimentation of the spent lime bath. Owing to the School's work time and to the necessity to have daily some permeate to prepare the lime bath, the spent bath were filtered after a simple screening.
- Low inlet presure. In the Italian tannery the pressure values were 5.2 bars (inlet) and 1.2 bars (outlet).
- Possible membrane clogging.

The values obtained in the second series of tests (especially n. 7 and 8) on spent baths after 4 hours sedimentation are closer to the Abcor specifications but lower than those achieved at the Italian tannery.
Probably this is due to some differences in the characteristics of the two unhairing baths and/or in the two plants' operational conditions.
Anyhow, the tests may be considered satisfactory, and the Brazilian Team will continue them in order to define optimal performances.
The tests at Estancia Velha had confirmed the following criteria:

i : the spent lime baths must be pre-settled before ultrafiltration;

ii : the optimum liquor temperature is near 40 °C and the flow inside the membrane 4-5 m/sec to reduce clogging;

iii : a careful cleaning of membranes is also necessary at the end of every working cycle;

iv : from 100 parts of initial raw lime bath may be expected 10-15 parts of pre-settled sludges, 10-15 parts of concentrate and 70-80 parts of permeate.

TABLE II - FIRST SERIES OF TESTS

Test N°	Treated liquid	Working Temperature	Inlet Pressure	Outlet Pressure	Permeate flow	Specific flow (°)	Remarks
-	Clean water	24 °C	3 bars	1.5 bars	200 l/h	190 l/m²h	flow control test
1	Spent unhairing bath	30 °C	3 bars	1.8 bars	62 l/h	49.5 l/m²h	indicative test on uncontrolled unhairing bath of the School
2	as above	30 °C	2.8 bars	1.5 bars	51 l/h	45.5 l/m²h	new bath according to the operational performance (pag.)
3	as above	30 °C	2.8 bars	1.5 bars	23 l/h	20.1 l/m²h	bath coming from 1 st recycle
4	as above	28 °C	2.8 bars	1.5 bars	37.5 l/h	34.6 l/m²h	bath coming from 2 nd recycle
-	clean water	24 °C	3 bars	1.5 bars	188 l/h	181 l/m²h	flow control test

The average values obtained are: (on spent unhairing baths)

- U.F. unit permeate flow = 43.4 l/h
- Membrane specific flow (°) = 37.4 l/m²h

TABLE III - SECOND SERIES OF TESTS

Test N°	Treated liquid	Working Temperature	Inlet Pressure	Outlet Pressure	Permeate flow	Specific flow (°)	Remarks
-	Clean water	24 °C	2.8 bars	1.5 bars	200 l/h	193 l/m²h	Clean water flow control test
5	Spent unhairing bath after 4 hrs sedimentation	24 °C	3 bars	1.5 bars	44 l/h	42.5 l/m²h	16 membranes
6	as above	40 °C	3 bars	1.5 bars	58 l/h	40.2 l/m²h	16 membranes
7	as above	28 °C	3.4 bars	1.5 bars	40 l/h	64.8 l/m²h	8 membranes
8	as above	40 °C	3.4 bars	1.5 bars	47 l/h	60 l/m²h	8 membranes

The average values obtained are: (on spent unhairing baths)

- U.F. unit permeate flow = 47.25 l/h
- Membrane specific flow (°) = 51.87 l/m²h

(°) = Standard conditions: 25 °C - 3.5 bars table IV: U.F. tests analytical data (average values)

	Sulphide S^{2-} mg/l	COD mg/l	TKN mg/l	Suspended Solids mg/l
Raw bath (°)	1,560	23,600	1,500	2,600
Permeate	1,225	6,950	550	56
Concentrate	1,335	54,400	3,775	18,735

(°): after presedimentation

The analytical data (see table IV) show an average reduction of 70% of COD, 93.5% of suspended solids and 100% ca of settleable solids. These data are similar to the mean values obtained in the afore mentioned tannery during two years of U.F. utilization:

- COD reduction = 80-32% ca;
- suspended and settleable solids reduction = 100% ca.

Comments

The U.F. of the spent unhairing baths is doubtless an excellent technique which permits a clear and constant reusable liquor.
This reduce considerably the inconveniences (grease stains, dirty grain, irregularity of the leather characteristics) sometimes occuring with the more simple "settling and reuse" technique.
On the other hand, the choice of the operational conditions and the membranes' maintenance represent, in our opinion, the biggest difficulty for a wide use of U.F. in tannery.

The money return from recovered chemicals (approx. 5-8% of $Ca(OH)_2$ and 25-30% of Na_2S) is low if compared to the investment and maintenance costs.
For example, in the afore mentioned tannery (60 tons of processed hides per day, 120-130 m^3 of spent lime baths treated per day, 60 m^2 of U.F. membranes surface, plant working 120 h/week with only one cleaning operation per week) the value of the recovered chemicals hardly covers the maintenance and investment costs (no profit).

This lack of profit is mainly determined by the membranes' life (max. 20 months) and their initial cost.
The advantages of this technique are more evident if one considers the effluents treatment cost aspect. As before said, this process provides a big COD and solids reduction and concomitantly an abatement of the effluents treatment costs.
The problem remains to find a system for treating the presettled sludges and the concentrate which are very difficult to dewater. At the moment a definite technique is not available, and we may only indicate some possible alternatives:

- proteins recovery;
- dewatering after heating;
- direct utilization in agriculture (no chrome in these sludges);
- anaerobic digestion.

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2.2.2 Flotation unit

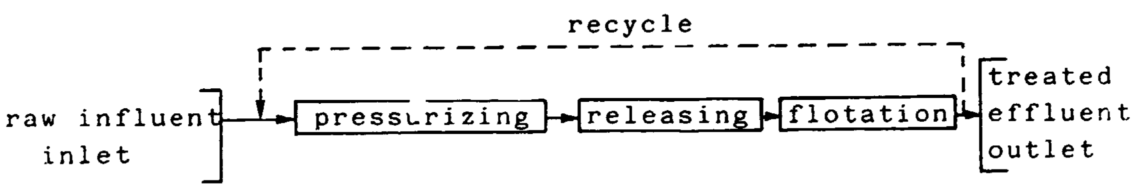
Equipment details

The unit is a Dissolved Air Flotation (D.A.F.) unit (see fig. 5) with the following characteristics:

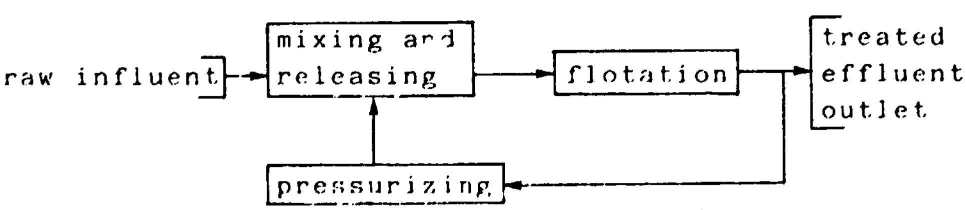
- pressurizing tank:
  . volume 140 l
  . max working pressure 6 bars
- pressure releasing tank:
  . volume 40 l
- net flotation zone:
  . Ø 160 cm
  . height 65 cm
  . surface 1.8 m^2
  . volume 1.2 m^3 ca.

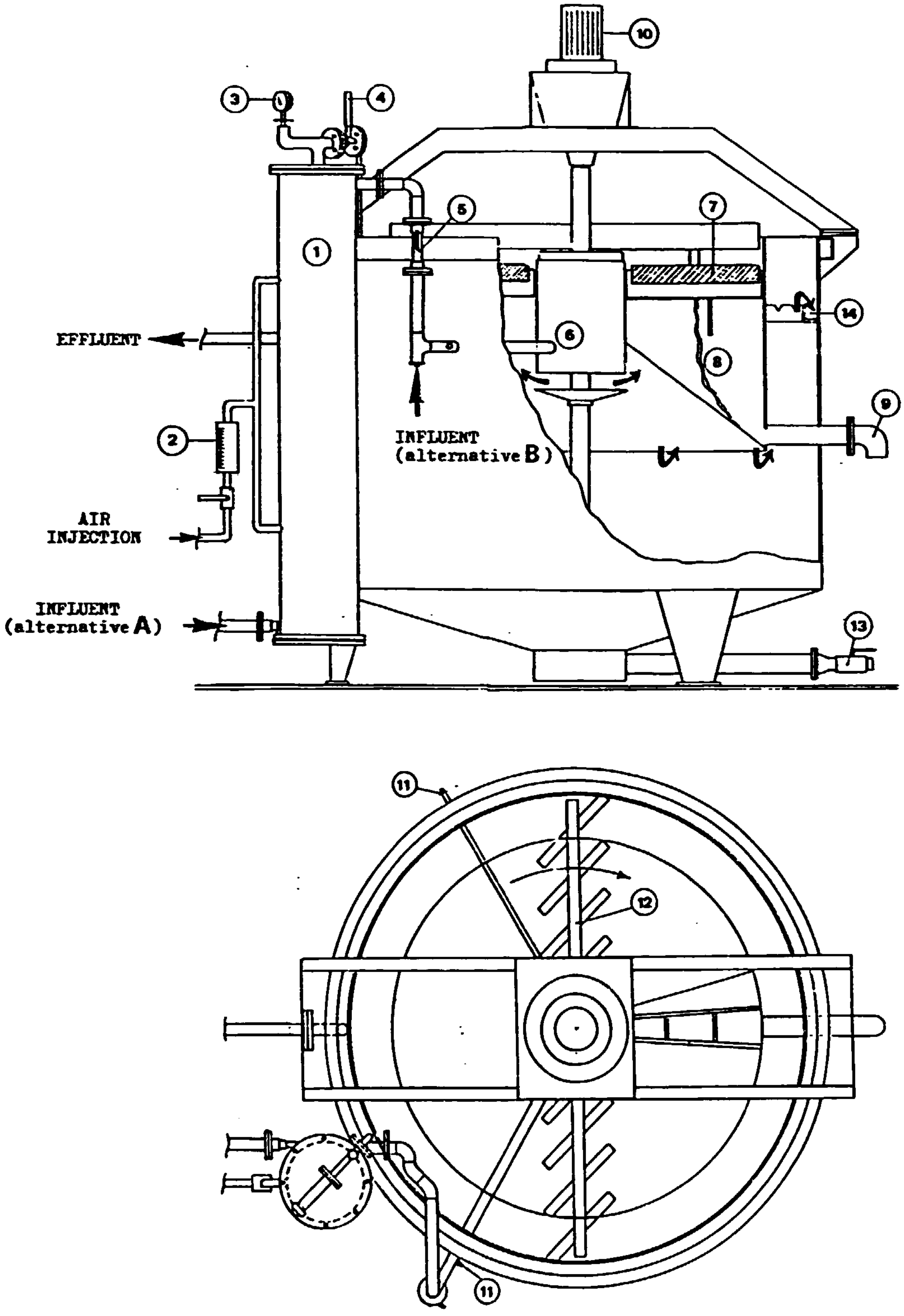
Two inlet points are foreseen:

- alternative A : the raw influent is pressurized with or without addition of part of the treated effluent according to the following scheme:



- alternative B: only the recycled treated effluent is pressurized and subsequently mixed with the raw influent before the pressure releasing zone:





1	Pressurizing tank	8	Floated sludge box
2	Air flow-meter	9	Floated sludge draw-off
3	Manometer	10	Motor and variable speed gear
4	Safety-valve	11	Chemicals addition points
5	Pressure reducing valve	12	Heavy sludge scraper
6	Coarse bubbles releasing zone	13	Heavy sludge draw-off
7	Floated sludge scraper	14	Effluent weir

figure 5

The flotation tank is equipped with a variable speed mechanical scraper for collection and removal of the surface and bottom sludges.

Other plant facilities

- Treated effluents recycle and holding tank:
  . volume 1,000 l
- wedge wire inclined screen (Hydrasieve type):
  . opening size (slot openings) 1 mm
  . surface 0.5 m^2
- air corpressor with flow-meter (0-500 Nl/h):
  . max. working pressure 10 bars
  . max. capacity 1,800 Nl air/h
- feeding pump, screw pump (Mohno type) coupled with electric motor 4 kW and variable speed gear (5:1):
  . capacity at 0 bars from 1.5 m^3/h (70 rpm) to 8.0 m^3/h (350 rpm)
  . max working pressure 6 bars.

Flotation tests

Since the unit was installed in the pilot plant at Estancia Velha near the beginning of November 1986, only a part of its possibie applications could be tested in the two remaining months of our activity in the Project area.
In these tests the flotation unit was employed in the primary treatment as a suspended solids removal device alternative to the sedimentation one.
The waste water from the external tannery were, after screening, homogeneization and sulphide oxidation, partially bypassed to the unit. (see fig. 6)
note to fig. 6: the two existing pumps were utilized only for a better use of the existing piping system and, further-

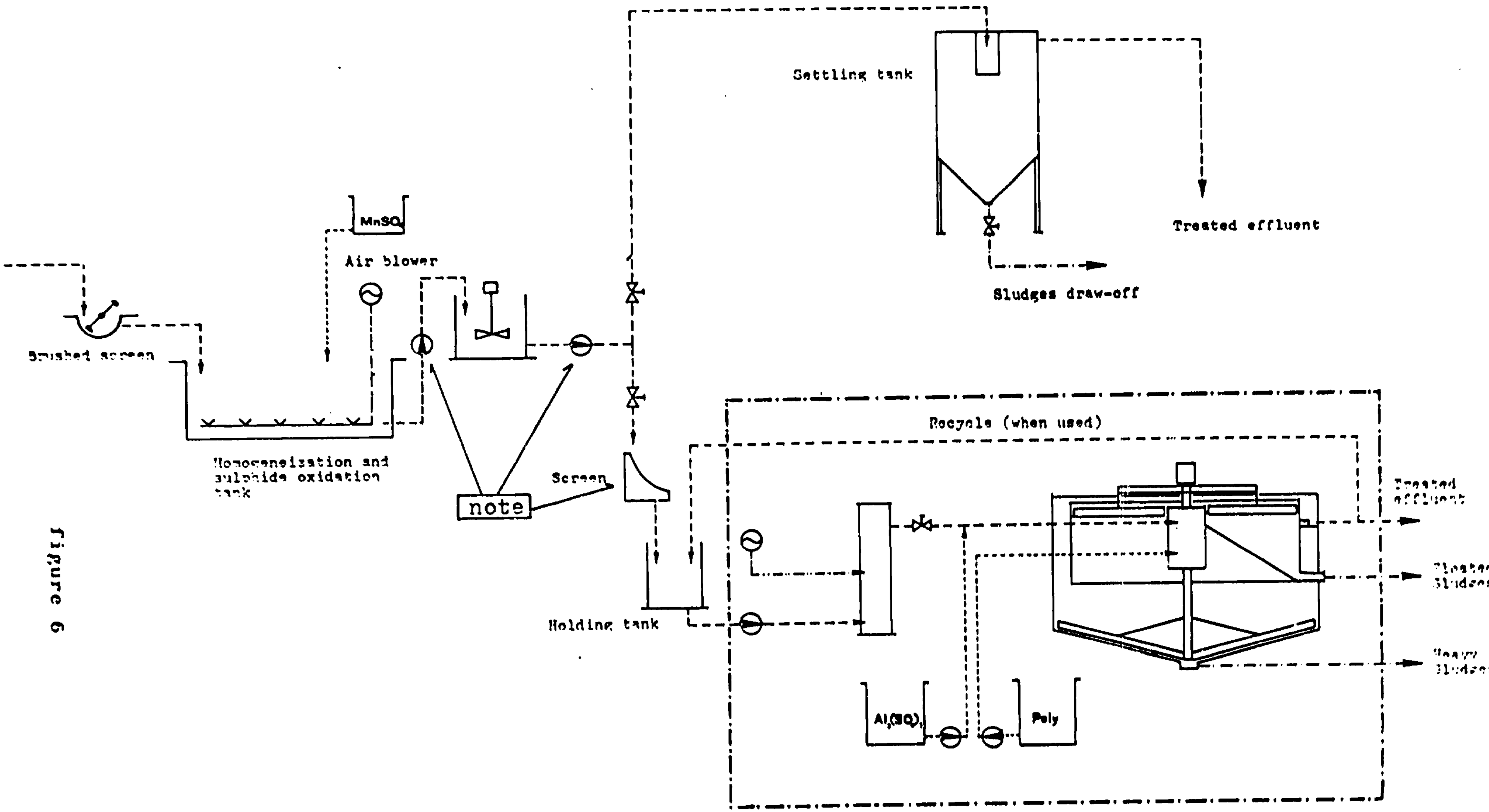

Brushed screen
Homogeneization and sulphide oxidation tank
$MnSO_4$
Air blower
note
Screen
Holding tank
Settling tank
Treated effluent
Sludges draw-off
Recycle (when used)
$Al_2(SO_4)_3$
Poly
Treated effluent
Floated Sludges
Heavy Sludges

figure 6

more, the second screen was installed more for security than need: an eventual full scale plant will be more simple.

Two series of tests were carried out according with alternative A:

test 1: a part of the treated effluent was recycled and mixed with the influent before pressurizing;

test 2: the raw influent was treated by direct pressurizing (no recycle).

The tests operative conditions are reported in table V.

table V

	TESTS 1	TESTS 2
Parameter	Range	Range
Raw influent, flow m^3/h	2.0 ÷ 2.9	3.6
Recycle, percent	50 - 100	---
Total flow, m^3/h (influent + recycle)	3.8 - 4.1	3.6
Air flow, Nm^3/h	0.30 - 0.45	0.05 - 0.10
Pressure, bars	5	2.5 - 3.0
Air to influent volume ratio, Nm^3/m^3	0.10 - 0.17 (°)	0.014 - 0.028
Air to solids ratio, kg/kg	0.04 - 0.10	0.008 - 0.016
Surface hydraulic loading, m^3/m^2h	1.1 - 1.6 (°)	2.0
Float Detention, min.	25 - 38 (°)	20
Detention in the pressurizing tank, min.	2.0 - 2.2	2

Note (°): calculated on the raw influent flow - recycle not included.

The suspended and settleable solids content and the COD of the raw influent and the treated effluent were analysed and, in the test 1, also compared with the data of the effluent from primary sedimentation. The mean values obtained are reported in table VI.

table VI

PARAMETER	RAW INFLUENT FROM EQUALIZATION TANK	FLOTATION EFFLUENT	REDUCTION PERCENT	EFFLUENT FROM SEDIMENTATION	REDUCTION PERCENT
TESTS 1 :					
Settleable Solids ml/l	102	0.4	99.6	1.0	99.0
Suspended Solids mg/l	2,680	640	76.1	430	83.9
COD mg/l	2,710	1,180	56.5	1,378	49.2
TESTS 2 :					
Setteable Solids ml/l	95	1.0	98.9	Note: no comparison data because all the raw influent was treated by flotation	
Suspended Solids mg/l	2,090	410	80.0		
COD mg/l	2,340	1,030	56.0		

Chemicals dosage

Test 1: different dosage of alum (up to 1,500 mg/l) were tested. The most suitable efficiency/cost ratio was found for a dosage near 300 mg/l. No polyelectrolyte dosage.

Test 2: the alum and polyelectrolyte dosages were respectively 300 mg/l and 0.5 mg/l.

Discussion of the results

The following preliminary conclusions may be drawn from results obtained in the Estancia Velha conditions:

i. flotation is an alternative technique well applicable to the primary treatment of tannery effluents;

ii. the process may be carried out directly on the raw influent (recycle is unnecessary, very probably because of the synergism of the surfactant substances held in the tannery wastes);

iii. the quality of treated effluent appears similar to that from a primary sedimentation save, perhaps, a higher content of suspended solids depending from the flocs shearing by the action of the pressurizing pump. For this, coagulant dosage (alum or iron salts) is advisable and must be added after pressurizing;

iv. the sludge blanket is not too stable: also under light shaking forces part of the floated cake easily settles; special attention must be given to the scraping mechanism configuration and speed. A dosage of polyelectrolyte improves this stability considerably.

The air flow control is also important: a high air flow induces turbulence. In fact during the test 1, a large quantity of the produced sludge (up to 50%) was settled, whereas in the test 2 no significant sludge deposit was noted.

The potential advantages of flotation in comparison with sedimentation are:

1. higher surface loadings, hence smaller tank size (important where space is critical). In the tests carried out a maximal surface loading of 2 m^3/m^2h and a retention time of 20 min resulted (it means a two-three times reduction of the tank size in comparison with clarifiers) but these values may not be considered the better performances; in fact during the test 2 all the waste waters flow from homogeneization tank was by-passed and treated by flotation (no more influent available to increase the flow).
2. Possibility, especially for small-medium tannery effluents

plants, of installing a package unit (pre-assembled) instead of more articulate and complex devices (important in areas in which specialized labor for the assembly is not available).

3. The dry content of the floated sludge is very high and comparable to that of a tannery primary sludge after thickening treatment. The dry content of the floated sludge in the test 2 varied between 4 and 10% on weight, with an average value of 6.2% against the average value of 2.5% (max. 3.3%, min. 1.1%) obtained by the primary sedimentation tank of the pilot plant in more than three years of work.

The principal disadvantages are:

1. higher investment and operation costs of the primary treatment; indicatively the coagulants consumption may be 50-100% more, and the energy consumption 10 times more.
2. Device that needs more care in operation and maintenance.

<u>Future activities</u>

The following work program with flotation unit will be undertaken by the Brazilian Team:

a. continue the tests according to alternative A without recycle, to check the better operating parameters including the upper hydraulic loading of the station (for this it is necessary to increase the influent flow);
b. test the alternative B;
c. test D.A.F. applications in secondary treatment and primary and secondary sludges thickening.

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3. TRAINING ACTIVITY

Since a high level of competence was achieved by the Brazilian Team of the Project during the first phase, training consisted principally in improving professional capacity and removing theoretical and practical doubts. This "experience transfer during the presence of the Italian Team in the Project area was continuous and capillary.
Some summary talks on the tannery effluents treatment in general were given to the new personnel of the Project.
As said before, the flotation and ultrafiltration processes were theoretically treated before starting the tests in the pilot plant. Furthermore particular emphasis was given, in accordance with the Project's aims, to the secondary (biological) treatments and to the disposal of the solid wastes in tannery.

3.1 Secondary (biological) treatments

In this second phase, all the aspects of the secondary treatments of tannery effluents were resumed and examined closely on the basis of the results obtained in the first phase (see our first phase Final Report).
Particular care was addressed to those biological treatments which seemed more adaptable to local conditions: the extended aeration activated sludges and the aerobic-facultative lagoons.
All the theoretical and engineering bases were fully explained; furthermore, the microbiological and biochemical aspects were treated by a qualified Italian expert (graduate in Biology) in a series of theoretical-practical courses. A summary of these courses is reported in Annex IV.
Two arguments of this activity deserve to be mentioned here.

Aerobic facultative lagoons dimensioning

Since there was uncertainty on the design parameters for the aerobic-facultative lagoons, they were calculated on the basis of the data obtained from the pilot plant lagoon (inlet and outlet BOD_5, water temperature etc.).
The biological kinetic of this kind of treatment may be represented by the following equation:

$$\frac{S_e}{S_o} = \frac{1}{1 + K_T t} \qquad \text{(a)}$$

where:

- S_e = outlet BOD_5, mg/l;
- S_o = inlet BOD_5, mg/l;
- t = detention time, day;
- K_T = substrate removal rate coefficient, day^{-1}

The experimental parameter to be defined to design a lagoon is K:

$$K = \frac{S_o - S_e}{S_e} \cdot \frac{1}{t} \qquad \text{(b)}$$

Furthermore K depends from the temperature, according to the following equation:

$$K_T = K_{20} \, \theta^{(T - 20)} \qquad \text{(c)}$$

where:

- K_T = substrate removal rate coefficient at T;

- K_{20} = substrate removal rate at 20°C;
- T = temperature of the lagoon;
- Θ = temperature coefficient, which is equal to:

$$\log \Theta = \frac{\log K_1 - \log K_{20}}{T_1 - 20} \qquad (d)$$

The values of K_{20} and Θ obtained substituting the lagoon's data in the preceding equations are:

$$K_{20} = 1.512 \text{ day}^{-1}$$

$$\Theta = 1.016$$

note: the specific installed power in the lagoon was 3.5 W/m^3.

These results has been successively utilized by the Project Personnel in lagoon dimensioning and also adopted by the D.M.A. (Departemento do Meio Ambiente) Technicians to evaluate the correct size for the lagoons projects submitted to their approval.

Nitrification and denitrification of tannery effluents

Ammonia nitrogen ($N\text{-}NH_4^+$) in tannery effluents derives both from the degradation of skin proteins (mainly keratins from unhairing baths) and from ammonium salts utilized in some processing phases (e.g. ammonium sulphate from deliming bath) and very often its concentration, even after a complete treatment (chemical-physical and biological) may be around 100-150 mg/l against a discharge standard which generally is 10-15 mg/l.

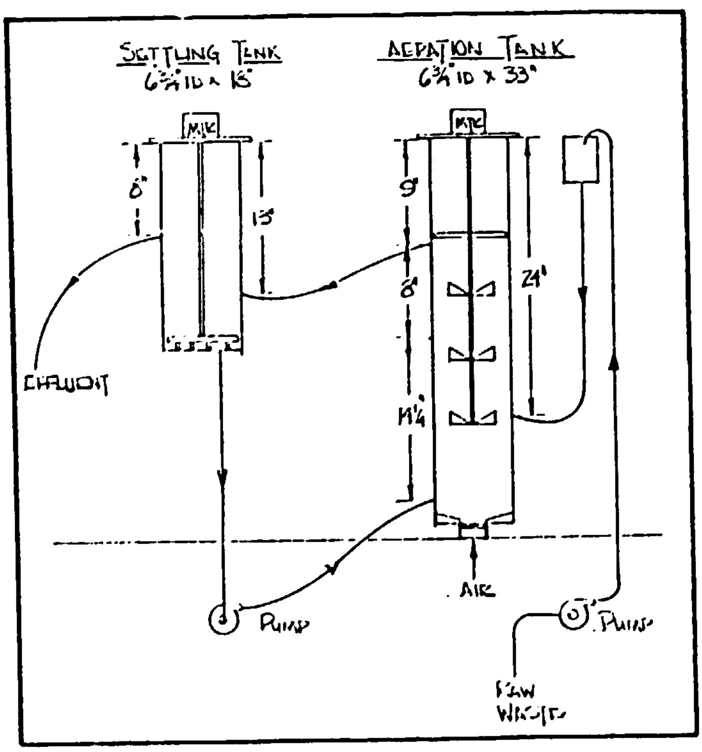
The removal system more frequently utilized are biological treatments in which the operative conditions are adjusted

so as to allow the "nitrification-denitrification", that is to say the microbial conversion of $N\text{-}NH_4^+$ to nitrate nitrogen ($N\text{-}NO_3^-$) - first step - followed by the conversion of $N\text{-}NO_3^-$ to nitrogen gas - second step.
Plants of this type are in action in several kinds of industry (e.g. fertilizer and agro-alymentary industries) and in the sewage treatment works. However, at present, no industrial plants to carry out this treatment in tannery exist, so there is a lack of data on possible operating conditions. For this reason, after the theoretical treatment of the topic, it was deemed useful both to start a practical series of tests using the laboratory equipment and to formulate a hypothesis of possible utilization of the pilot plant for nitrification-denitrification.

a. Laboratory tests

In these tests, which are now going on, the bench scale activated sludge plant of the laboratory (see fig. 7) is used, fed with the effluent from the primary treatment of the pilot plant.

figure 7: bench scale apparatus



The operative conditions used are those typical of an extended aeration plant which ought to be the most favourable for obtaining nitrification:

- influent flow 400 ml/h
- " BOD_5 500-700 mg/l
- " $N-NH_4^+$ 100-150 mg/l
- total organic loading 4.8-6.7 g BOD_5/day
- total $N-NH_4^+$ loading 1.0-1.5 g $N-NH_4^+$/ day
- retention time 34 h
- MLSS 4,000 mg/l (adopted)
- volatile sludge content 60% (adopted)
- sludge recycle 100% (adopted).

The results obtained after a 25 days plant running show that the nitrification has started; in fact, there is a gradual increasing of $N-NO_3^-$ and a reduction of $N-NH_4^+$ in the effluent.

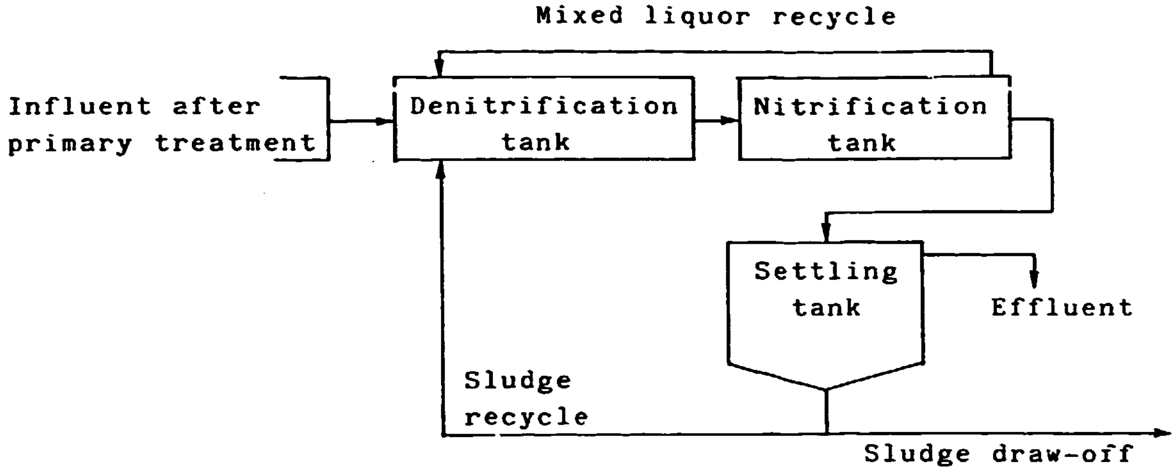
Naturally, this first period was too short to draw precise conclusions so the tests will be carried on by the Brazilian Staff in the next months.

b. Pilot plant tests

The possibility of using the pilot plant to make tests of $N-NH_4^+$ removal, was weighed. The two processes steps require different operative conditions, and separate basins for nitrification (aerobic process) and denitrification (anoxic process) are utilized.

The most common flow sheet is the following in which the influent is mixed with the recycled sludge and the recycled mixed liquor into the denitrification tank. (see next page)

According to this scheme, a new arrangement of the pilot plant's biological phase facilities was hypothesized utilizing



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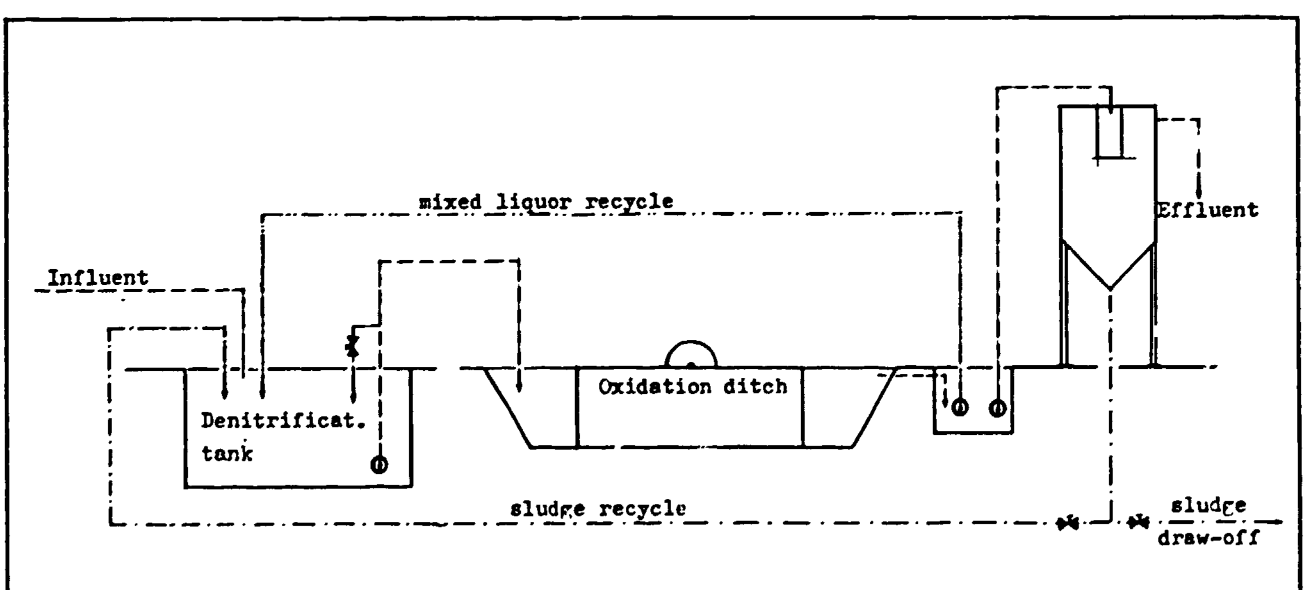
the oxidation ditch for nitrification and a tank actually used for a conventional activated sludge treatment, for denitrification; (see fig. 8)

figure 8



Operative conditions:

- influent flow 1 m^3/h
- influent $N\text{-}NH_4^+$ 100-150 mg/l
- influent BOD_5 500-700 mg/l
- total $N\text{-}NH_4^+$ loading 2.4-3.6 kg $N\text{-}NH_4^+$ /day
- total organic loading 12-16.8 kg BOD_5/day.

Oxidation ditch:

- tank volume 60 m^3 ca
- retention time 60 h
- MLSS 3,600 mg/l
- sludge loading 0.07 kg BOD_5/kg MLSS day (adopted)
- volatile sludge content 60% (adopted)
- oxygen requirement 1.8 kg O_2/h ca (calculated, **see note**).

Recycles:

- sludge recycle 100% (adopted)
- mixed liquor recycle 400% (adopted).

Denitrification tank:

- tank volume 10 m^3 (regulated by floating switch)
- retention time 10 h.

note: oxygen requirement calculation

$$O.R. = \frac{(\Delta BOD_5 \cdot a) + (b \cdot SVC \cdot MLSS) + (\Delta N\text{-}NH_4^+ \cdot c)}{24}$$

where:

- ΔBOD_5 = BOD_5 removed (90% adopted) = 13 kg BOD_5/day
- a = oxygen utilized for BOD_5 oxidation = 0.8 kg O_2/kg BOD_5(adopted)
- b = oxygen utilized for endogenous respiration = 0.15 kg O_2/ kg MLSS per day (adopted)

- SVC = volatile sludge content = 60% (adopted)
- MLSS = mixed liquor total suspended solids = 216 kg (adopted)
- $N\text{-}NH_4^+$ = $N\text{-}NH_4^+$ removed (90% adopted) = 2.7 kg $N\text{-}NH_4^+$
- c = oxygen utilized for nitrification = 4.57 kg O_2/kg $N\text{-}NH_4^+$ (adopted)

$$O.R. = \frac{(13 \cdot 0.8) + (0.15 \cdot 0.6 \cdot 216) + (2.7 \cdot 4.57)}{24} =$$

$$= 1.8 \text{ kg } O_2/\text{h ca.}$$

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3.2 Disposal of tannery solid wastes

The tanning industry produces large quantities and varieties of solid wastes; the disposal of these materials is, in our opinion, a problem difficult to solve, more difficult than the effluents treatment one.

As an example, in table VII are reported the data on the solid wastes produced by an Italian upper leather (bovines) tannery.

table VII : solid wastes from 1 ton of processed hide

Type of waste	quantity, kg	humidity % (on weight)	dry material, kg
Salt (hide sectioning)	15 - 20	-	15 - 20
Green trimming	32 - 35	40 - 45	18 - 20
Lime-fleshing	80 - 100	70 - 80	18 - 27
Shaving	120 - 130	55 - 65	44 - 56
Buffing dust	10 - 20	15	8.5 - 17
Blue split trimming	48 - 50	50	24 - 25
Grain trimming	8 - 10	15 - 20	7 - 8
Effluents treatment plant sludges (°)	2,000	92 - 94	120 - 160
Other wastes	15	60 - 70	4 - 6
Total weight, kg	2,328 - 2,380	-	258.5 - 339

(°) after thickening

It must be emphasized that from one kilo of processed hide, 2.3 kg ca of wastes are produced (this quantity may be reduced to 0.7 kg if the sludges are dewatered up to 35% dry material cake).
Research carried out in 1982 by the METROPLAN (Fundaçao Metropolitana de Planejamento) on the tanneries located in the Vale do Sinos, R.S. (around the Project area), results in a 58 tons/day production of solid wastes from 13,000 daily processed hides (325 tons/day ca). See table VIII.

table VIII : solid wastes produced by tanneries in Vale do Sinos.

Municipality	production (hides/day)	solid wastes, Ton/day
Novo Hamburgo	4,780	21.5
Estancia Velha	4,175	18.8
Sapucaia do Sul	2,150	9.7
São Leopoldo	1,779	8.0
Campo Bom	100	0.4
Total	12,977	58.4

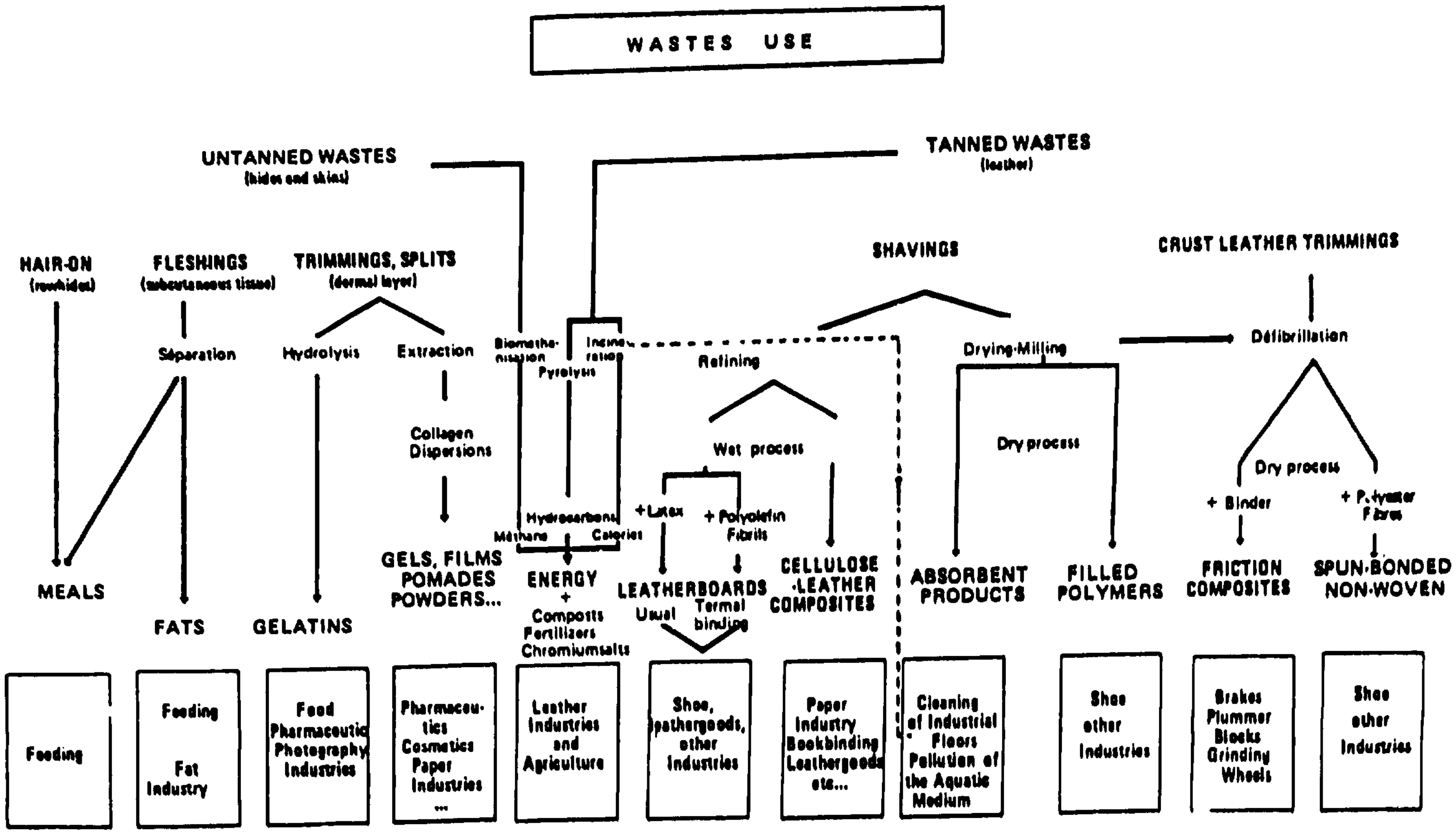
This figure (17.8% of the weight of processed hides) does not consider the production increase since 1982 and furthermore, does not include fleshing. In fact, most of the Brazilian tanneries make a partial grease recovery from fleshing; neverthless the employed method (dissolution with direct steam or by autoclave - surnatant grease recovery and subnatant liquors discharge) is a only means to eliminate this waste rather than a real recovery system; consequently, with the construction of effluents treatment plants, it may become uneconomic because of the high costs for the treatment

of the discharged highly polluted liquors.
Furthermore, there has been a sensible increase of solid wastes with the introduction in Brazil of treatment plants for tannery effluents. Calculating on the same quantity of hides a 15% of sludge as dry material, result 5 tons/day of sludge, i.e. 125 tons/day of liquid sludge (4% on dry material).
It is necessary to distinguish between process solid wastes and effluents treatment sludges in dealing with the final disposal of these materials.

a. Process solid wastes

There are several techniques for their complete reuse. An outline of the possible use of these materials is reported in scheme 1.
Many Brazilian industries utilize tannery wastes as raw material for their production; the above-mentioned research of the METROPLAN reports that almost the totality (70-80%) of these wastes is withdrawn by specialized industries and the remainder (20-30%) is burned or disposed on land (sanitary landfill and/or uncultivated lands).
Recently, the imposition of improved sanitary regulations has made the final disposal of such wastes more difficult and has shown the need of improved methods to reuse these materials. The Sanitary Authorities has forbidden disposal by burning (widely utilized) both to prevent air pollution and possibly toxic substances in the residual ashes (e.g. chromium).
Consequently both an increase in the number of industries which utilize these materials and the creation of areas by the Sanitary Authorities (landfill) where these wastes may

Scheme 1



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be disposed are highly to be recommended.

b. Effluents treatment sludges

These wastes are those which present the biggest problems for final disposal. Although several technical solutions to reuse these materials have been proposed, until now no large scale solution exists; the only disposal method used is landfill.

Among the alternative solutions, the best known are:

- in agriculture, as fertilizers;
- in brick production;
- in anaerobic digestion (bio-gas production).

The last two alternatives, in our opinion, will improbably represent the final solution of the problem both for technical and economical reasons.

Whereas the possibility of brick production use of tannery sludges (10-15% on clay weight) has been proven, the economical validity of this process is still in doubt.

The sludge treatment by anaerobic digestion does not seem to be, for the present, a technique economically applicable on industrial scale because of the high content of inorganic matter and the presence of potentially toxic substances (e. g. Cr^{3+} and Sulphates) in the sludge.

Consequently, the only alternative whose recent progress (even if still on experimental level) deserves to be mentioned is the use in agriculture.

Furthermore this solution is, in our opinion, particularly suitable to the local Brazilian conditions (large country areas); it could prove, if well carried out and controlled, the closing of the "production-depollution" circle.

The agricultural use of residual sludges is widely adopted in European Countries: in the German Federal Republic 43%

of the sludge is employed in agriculture, in France 23%, in Denmark 45%, in the United Kingdom 45% and in Luxemburg 90%. The fundamental reason for the choice of this kind of disposal is its low cost in comparison with other systems and its offering the possibility of recovering valuable agricultural resources: organic matter and fertilizing elements (essentially N and P) contained in the sludge.

On the other hand, industrial sludges present a drawback: they may contain noxius substances which are pollution risks both for agricultural and the general environment and therefore they must be evaluated costantly.

The most recent information about agricultural use of tannery sludges concerns the results obtained in Italy after a parallel two-year experiment carried on by the Universities of Pisa and Piacenza and financed by two important joint treatment plants for tannery effluents located in Tuscany (S. Croce sull'Arno and Ponte a Egola). Table IX reports the characteristics of the sludges produced by these plants.

table IX

Parameters	S.Croce sull'Arno a	Ponte a Egola b
Total Residue on Evaporation at 105 °C, %	38.3	32.0
pH (in H_2O)	9.1	7.8
Total Fixed Residue (550 °C), % (°)	61.0	57.2
Total Volatile Residue (organic matter), %(°)	39.0	42.8
Organic Carbon (Springler-Klee), % (°)	21.0	22.0
Total Nitrogen, % (°)	2.1	2.2
Total P_2O_5, % (°)	0.42	0.40
Total K_2O, % (°)	0.01	0.023
Total $CaCO_3$, % (°)	41.4	38.1
Chromium VI (°)	absent	absent
Total Chromium (extraction with HCl 6N), %(°)	2.23	0.33
Sludge dewatering system	filter-press	band-press

a : centralized plant treating for the most part chrome tanneries effluents.
b : " " " " " " " vegetable " " .
(°): on Dry Substance

The cultivations subjected to treatment were: Indian corn, wheat and rice, and the quantities of sludge employed as fertilizer were on an average of 40 tons/hectare (one application).

The first results of these tests have been recently published with the prudence due to their being preliminary data:

I the fertilizing value of tannery sludges is not negligible: two plants treated with sludge (A) have shown a production larger than the control plants (0 - no fertilizer) even if lower than the plants (B) treated with the same quantity of N but utilizing a mineral fertilizer; the proteic content follows the same relation: $0 < A < B$.

II The chromium content in the plants (0=A=B) remains within physiologic values so an accumulation of chromium has not occurred (perhaps with the exception of the roots).

III The water of soil leaching has shown a N content bigger for the soil treated with mineral fertilizer than for those treated with sludge ($0 < A < B$), that is to say that in the soil treated with sludge there is an accumulation of N and, consequently, the sludge has slower and more protracted fertilizing effects.

IV The chromium content of the soil has shown an increase (particularly using the sludges of S. Croce sull'Arno) in comparison with the soil treated with mineral fertilizer ($0=B < A$). For this reason more and more efficient methods to detain the chromium in tannery (high exhaustion tanning methods and/or chromium recycle) are recommended in order to limit the chromium content of the sludge.

Furthermore this agrees with the sanitary regulations of many Countries which set limits to the maximum quantity of chromium disposable onto the soil (see table X).

table X : use of chromium-containing sludges on land. European acceptance levels

	Max Cr content of sludge, mg/kg	Max Cr content of soil, mg/kg	Cr added to soil kg/ha per years
Italy	500	50	2/ year
France	200	150	30/ 10 years
Switzerland	1,000	-	-
Germany (W)	1,200	100	-
Poland	1,000	-	-
Holland	500	-	100/80-100 years
Sweden	1,000	-	1/ year
Finland	1,000	-	4/ year
United Kingdom	-	-	1,000/30 years
E.E.C. directive (proposed)	750	50	100/10 years

It must be emphasized that in using industrial sludge in agriculture both the technical-agricultural as well as the sanitary aspects must be considered.

At the moment Brazil has no regulation on industrial sludges and their destination; however, it would be advisable that an experimentation similar to that in course in Italy and other European Countries (France, U.K. etc) begins soon in Brazil too.

Landfill

As afore mentioned, this is the system of solid wastes disposal most used in Italy. Generally, this methods is imperative, imposed by the Italian Sanitary Authority regulations. The E.E.C. directives on the disposal of solid wastes contai-

ning toxic and hazardous substances (E.E.C. directive 28.
03.78 n.73/319) lists a series of toxics that generally are not present in tannery sludges (Cr^{3+} is not included), so the restrictive directives of the Italian Sanitary Authorities, which impose high-safety landfills, is explained more by a prejudice against tannery sludges than by their toxicity.

The Italian local situation - densely inhabited areas, high seismic zones, many torrent-like rivers flowing into the Mediterranean (enclosed sea with slow water replacement) - only partially justifies this rigour.

In fact the disposal of tannery sludges is authorized only in high-safety landfills which have high implantation and maintenance costs. The expences for this service depend on the tannery location (distance from the landfill - carriage costs) as weel as on the landfill rates which vary from 15 to 25 U.S. Dollars per ton of sludge.

Furthermore, in some landfills, sludge with a dry matter content lower than 35% are not accepted and so, in this case, tanneries that have installed band-presses are obliged to effect a CaO dosage on the sludge cake in order to increase the dry matter (or to change the equipment with a filter-press).

A further problem is the landfill location; Municipalities preposed for this choice often come under pressure from citizens' committees (many people fear landfills almost as much as atomic power plants) so creating the needs for more and more guarantees and higher and higher costs.

For these reasons, it is commonly held that landfill is only a preliminary phase, one necessary for the lack of definitive technical solutions at the present moment.

It is unrealistic to start with a politics of effluents treatment without having an exit for the produced sludges. In the Brazilian situation, which is quite different from the European and particularly the Italian ones, landfill may represent, in our opinion, a transitory solution acceptable both from a technical and economical aspect.
Our activity in this field was to make a critical analysis of the legislation operative in Italy and to give general information on the constructional and safety aspects of landfilling.
These arguments were illustrated by a geologist of the Italian Team since most part of them pertain to Geology:

- landfill site selection:
  . geologic analyses;
  . geotechnical analyses;
  . hydrogeologic analyses;
- sludge characterization;
- conventional methods for controlled landfilling;
- ground waters protection and analyses.

A detailed summary of these arguments is reported in Annex V.

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3.3 Study tour

In the area of training activity may also be considered the assistance furnished by the Italian Team during a study tour effected in Europe in September - October 1985 by three Brazilian members of the Project Staff:

- Mr. Paulo JOST (chemical engineer- National Coordinator);
- Mr. Frederico WEBER (chemist);
- Mr. José Luiz ROSENBACH (chemical engineer).

During the Italian itinerary of this tour, accompanied by the Italian Team Leader, they visited:

1. S. Croce sull'arno: centralized plant (400 tanneries + municipal effluents) - Passavant;
2. S. Croce sull'Arno: chrome recovery centralized plant (150 tanneries) - Agip Nucleare;
3. Nuova David: tannery effluents treatment plant - Idronova;
4. Organazoto: fertilizers from chrome shavings - own technology;
5. Lapi S.p.a.: greases and proteins recovery from fleshing - own technology;
6. Salami S.r.l.: tomato juice factory, biological treatment with liquid O_2 - Siad;
7. Florence municipal plant for drinking water - Degremont;
8. Italprogetti S.r.l.: equipments for tannery and tannery effluents treatment;
9. Gozzini S.p.a.: equipments for tannery;
10. Ponte a Egola: centralized plant (150 tanneries + municipal effluents) - Acqua;
11. Ponte a Cappiano: centralized plant (15 tanneries) - Passavant and Termomeccanica;
12. Otto S.r.l. ecologica: band-presses and other equipments for treatment plants;

13. Spaccatrice Arzignanese (wet blue tannery): chrome recovery, sulphide recycle by ultrafiltration and effluents treatment plants - Studio Tecnico Dr. G. Clonfero;
14. Arzignano, Chiampo and Montorso: centralized plant (500 tanneries + municipal effluents) - Passavant, Termomeccanica and CPC;
15. I.C.E. (chrome tannery): chrome recovery and effluents treatment plants - Studio Tecnico Dr. G. Clonfero;
16. Gruppo Conciario Bassanese (chrome tannery): chrome recovery with MgO and effluents treatment plants - Studio Tecnico Dr. G. Clonfero;
17. Presot (sole tannery): effluents treatment plant - Studio Tecnico Dr. G. Clonfero;
18. Cogolo S.p.a. (chrome tannery): chrome recovery and effluents treatment plants - own technology.

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4. LABORATORY ACTIVITY

During this second phase of the Project, the laboratory has been daily engaged in the control analyses of the pilot plant and of the samples of waste water (on the average of 3-4 for week) sent by external tanneries.

Here are reported the activities in which the Italian Team Technicians directly intervened, both to support new tests in the pilot plant and to complete theoretical courses.

4.1 Analytical control of the ultrafiltration tests on spent unhairing baths

During the ultrafiltration tests it was necessary to make a considerable quantity of analyses on the feeding bath, the permeate and the concentrate, in order to verify the effectiveness of this technique. Some of the analyses were routine analyses in the Project laboratory, on the contrary the analysis of sulphides requested a preparatory setting up.

In fact the standard method (sulphides are stripped from the acidified sample with an inert gas - N_2 or CO_2 - collected in zinc acetate solution and then titrated with iodine) involve enough complex equipments and long execution time, so more practical and rapid alternative methods were tested:

a. direct iodometric method;

b. titration with Potassium Ferricyanide (1);

c. titration with Mercury Acetate.

The results are reported in tables XI and XII

table XI : solution 10 g/l ca of $Na_2S \times 9\ H_2O$

Method	S^{2-} mg/l	per cent deviation
a	2,738	+ 6.6% (Note)
b	2,512	- 2.3%
c	colour change point not well appreciable	
Standard	2,572	-

note: in this case we also precipitated the S^{2-} with Zinc Acetate and determined the sulphides by difference between the total I_2 consumed by the solution without precipitation of S^{2-} and I_2 consumed after precipitation of S^{2-}.

table XII : sample of spent unhairing bath of the School

Method	S^{2-} mg/l	per cent deviation
a	3,056	+ 27.3%
b	2,176	- 9.3%
c	colour change point not well appreciable	
Standard	2,400	-

On the ground of these tests, the titration method with Potassium Ferricyanide, was considered acceptable to control the sulphides in the spent unhairing baths and was also employed in the ultrafiltration tests.

References

(1) Jour. Amer. Leath. Chem. Ass. - Vol. 53, n.5 - Oct.1977.

4.2 Course of practical microscopy

This course had the aim of preparing the Brazilian Project personnel in the correct use of the microscope (magnifications, illumination, staining procedures etc.) to analyse and control the performances and the "state of health" of a biological treatment. Practical exercises were executed in laboratory on the following arguments:

a. the microscope: objectives (air and oil immersion) - eyepieces - light sources (lamp, condenser and diafragm) - mechanical parts - microphotography - measurement with microscope (eyepiece micrometer and stage micrometer slide) - phase contrast and dark field observations;

b. microscopical preparations: (the material to prepare the slides were drawn from the biological phase facilities of the pilot plant)
   - living organisms observation: vital staining and examination in hanging drop of Protozoa, Algae and Fungi;
   - permanent preparations of Bacteria of activated sludge: preparation, fixation, staining and mounting of wet smears (simple staining: methylene blue, carbol fuchsin, safranin, gentian violet and lugol; complex staining: Gram stain, capsule stain, slime layer stain).

4.3 Ground waters analysis

As complement of the applied geology course it was treated the control of ground waters since it involves analytical methods generally different from those utilized for waste water analysis. In fact the physical, chemical and biological quality of ground waters, generally change very slowly. For this reason, to prevent an eventual contamination it is necessary to value series of analytical data taking into consideration small differences of values among the various groups of parameters. Tha sampling and the analytical procedure must be very accurate, swift, reproducible in order to avoid wrong interpretation.

The parameters most commonly analysed are:

- Alkali, Alkaline Earth and Heavy metals;
- Sulphate;
- Chloride;
- Carbonate and Bicarbonate;
- Nitrite and Nitrate;

- Phosphate;
- Silica;
- Fluoride;
- Ammonia;
- Boron.

The analytical methods for the determination of these parameters were described in detail and some practical tests were made in laboratory.

Furthermore, to control a ground water analysis it is important to consider the Anion/Cation balance, that is to say that the summation of total negative charges (Anions) and the summation of positive ones (Cations) must not differ more than 5%.

Another method to test the accuracy of an analysis is to compare the Anion/Cation balance (mEq/l) with the Electrolytic Conductivity at 25 °C (mSiemens), the Anion/Cation balance must be about ten times the Conductivity:

$$\sum \text{Anions (mEq/l)} - \sum \text{Cations (mEq/l)} = 10 \times \text{Conductivity (mSiemens)}$$

Note:

- $\sum$ = summation.

References

E.P.A. - Seminar Publication: Protection of Public Water Supplies from Ground-Water Contamination - Environmental Protection Agency - 625/4-85/016; Washington 1985.

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5. EXTENSION SERVICE

5.1 External services to tanneries

In the second phase, the Project activity directed towards the Brazilian tanneries outside Rio Grande do Sul was remarkably increased. In the meanwhile, in fact, other Brazilian States had prepared their own regulations for waste water discharge; the lack of local specialists in tannery effluents treatment counselled a Project's assistance also in those States where significant tanning activity exists.

The major component of the Project activity in R.S. was in the area of secondary treatments; the first phase was spent in the implementation of the primary treatments often poorly designed and dimensioned (a secondary treatment cannot operate without a reasonably efficient primary unit).

Following the publicity received by the first phase and the action of the Sanitary Authorities who were increasing their pressure to make tanneries comply with discharge regulations, a massive increase in demand for assistance with individual tannery projects characterized this second phase. The tanneries' requests have almost outstripped the availability of the Project personnel.

More than hundred factories were visited and investigated and something like 70 outlines of effluents treatment projects or projects modification prepared; near 30 of these outlines have been detailed at the moment and transformed into executory plant projects by the Brazilian Team, and other 10 are in course of preparation.

The list of the visited factories from 1983 to 1986, in R.S. and in other Brazilian States is reported in Annex VI.

A detailed plant study that foreseen various alternatives of treatment has been taken as typical case and reported in Annex VII.

The projects were prepared according with the needs of the tanneries and the existing local situation.

The equipment foreseen in the plant projects is available on the Brazilian market (see table XIII) and much of it is on an European level of reliability and performance. The equipment is the same utilized in the pilot and demonstration plant at Estancia Velha. We have encountered some problems only with oxidation ditch rotors which are not easily available in Brazil. For this reason the secondary treatments employing oxidation ditch were seldom proposed even if this unit works very well in the pilot plant.

We did not have particular difficulties in project design even though existing facilities were not always adaptable to rational utilization.

The tanners are aware of the need to safeguard the environment but they think that the treatment efficiency level must be proportional to the real pollutional impact of the tanneries. Many tanners agree with chrome and sulphide recycle (philosophy of recycling in Brazil is more diffused than in Europe) so, in general, they want to install first these pre-treatments and successively the primary and secondary ones.

As regards the secondary treatments generally they prefer, when possible, the aerated or aerated/facultative lagoons.

The sludges dewatering and disposal (as happens in every tannery in the world) is the biggest obstacle to overcome:

- the sand beds (where location is favourable and area available) are suitable, also considering the Brazilian climate, only for tanneries up to a maximum of 10,000 kg of processed hides/day (1,500-2,000 m^2 of beds circa), factories of this dimension are uncommon in Brazil where 20,000-30,000 kg/day is the most representative production;

- the sludge mechanical dewatering (filter or band presses), at the present, implies in Brazil very high investment costs that may be supported only by industries with large production (more than 40,000 kg/day, not very common).

Considering that the solution of the sludges problems is essential for the success of every effluent treatment plant, sometime more simple and economic sludge disposal system were proposed for tanneries placed in isolated zones with large availability of uncultivated land: the sludge ponds. This solution, which can be criticized from strictly technical standpoint, may be tried in order to overcome the problem temporarily.

In our opinion, plant costs limitation is essential in Brazil in any realistic approach to tannery effluents problems. At the present the Brazilian leather industry has some difficulties (lack and high prices of raw hide, necessity of improving production to make head against international competition). For this reason, all investments are now directed to improving production; in future, when this situation will be overcome, the leather industry will also be able to face the costs of effluents treatment plants at European levels of efficiency. But now, in our opinion, to press for an unrealistic strategy in tackling the pollution problems would be not only unproductive but could even produce the opposite effects, indeed, technical and economical difficulties could provide an alibi for some tanners for not doing what they can and must do.

We believe that the Brazilian Government could encourage the tanners' efforts by means of economic aids (low interest rate, financings, subsidies to industry etc.) as happens in other countries.

In fact the only flaw of the Project's success is linked to the delay in the plant's installation (only three of more than 70 projects are at the moment installed and operational); this delay must be principally imputed to the high plant installation costs. Other causes (lack of experiences in the tannery effluents treatment, sometimes ambiguous regulations, Sanitary Authorities' bureaucracy etc.) may be considered only secondary causes.

This delay has had two negative effects:

- the lack, for the Brazilian Team, of a practical verification of the validity of the dimensioning parameters utilized in the projects and of a direct experience in implementation and operation of full-scale plants;
- the accumulation of a large number of projects which will be probably realized all at the same time, so that an accurate assistance service to the tanners in this important phase will be impossible.

The Project's activity of serving as liason between Local Authorities and tanners was also strongly increased in the second phase.

Each Brazilian State has its own institute designed to safeguard the environment, and their regulations are often at odds. Apart from the D.M.A. (Departemento do Meio Ambiente) in R.S., with whom the Project personnel had continuous technical exchanges, we met with many other State Environmental Institutes to illustrate the Project's aims and activities. Discussing technical solutions, we also outlined difficulties in making the tannery effluents comply with existing legislation .

Outside Rio Grande do Sul, the following Institutes were contacted:

- CRA (Centro de Recursos Ambientais) Bahia;
- SUREMA (Superintendencia de Recursos Hidricos e Meio Ambiente) Paranà;
- CETESB (Companhia de Technologia de Saneamento Ambiental) Sao Paulo;
- FATMA (Fundacao de Amparo a Tecnologia e Meio Ambiente) Santa Catarina;
- FEEMA (Fundacao Estadual Estudo Meio Ambiente) Rio de Janeiro;
- CPRH (Companhia Pernambucana de Recursos Hidricos) Pernambuco;
- COPAM (Companhia Protecao do Meio Ambiente) Minas Gerais.

table XIII: TANNERY EFFLUENTS TREATMENT
List of the equipment and their availability on Brazilian market

Equipment	Usage	Availability & suppliers	Performances & reliability	Cost
Screens				
- manual	coarse solids removal	tannery own production	++	°
- self cleaning (wedge-wire)	solids removal	Yes (^)	+++	°°°
- brushed	solids removal	Yes (^)	+++	°°°
Pumps				
- submersible	lifting & pumping in general	Yes (^^)	++++	°°
- helicoidal	sludges & pumping in general	Yes (^^)	++++	°°
- centrifugal	pumping in general	Yes (^^)	+++	°°
- dosing	coagulants dosing	Yes (^^)	++	°°
Electric stirrers				
- slow speed	flocculation & chemicals dissolution	Yes (^)	++++	°°°
- high speed	chemicals dissolution	Yes (^^^)	+++	°°
Fibreglass tanks	chemical storage and dissolution	Not so easy	++	°°°
Vertical sedimentation tanks	Primary sedimentat. and sludge thickening	Yes only in steel (not in fibre glass)(^^^)	++	°°
Submersible mixers	Sludge conditioning, spent lime baths mixing etc.	Yes (^)	++++	°°°
pH-meters	pH control	Yes (^^)	++	°°

Cont.

Blowers - centrifugal	sulphide ox., equalization, sec.treatment	Yes (^^)	+++	oo
- lobe rotors	sulphide ox., equalization, sec.treatment	Yes (^^)	+++	ooo
Air diffusers - coarse bubbles (non-clog)	equalization	Yes (^^^)	++	oo
- medium and fine	sec.treatment	Yes (^^)	++++	ooo
Surface aerators - high speed	equalization, sulphide ox., sec.treatment	Yes (^^^)	++	oo
- low speed	equalization, sumphide ox., sec.treatment	Yes (^^)	+++	oooo
Rotors for ox.ditch	sec.treatment	No generally imported	++++	oooo
Scrapers for circular clarifier	primary & secondary sedimentation	Yes (^^)	+++	ooo
Scrapers for sludge thickener	sludges thickening	Yes (^^)	+++	ooo
Filter presses	sludge dewatering	Yes (^)	+++	oooo
Band presses	sludge dewatering	No generally imported	++++	oooo

Performances and reliability :

++++ = very good
+++ = good
++ = fair
+ = poor

Local potential suppliers :

^^^ = many
^^ = enough
^ = few

Cost(in comparison with the european one)

oooo = very high
ooo = high
oo = equal
o = low

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5.2 Miscellaneous activities

a. From 11 to 13 September 1985 a meeting on industrial solid wastes (I° Encontro Sobre Residuos Solidos Industriais) took place in Porto Alegre, R.S.. The meeting was organized by CIENTEC (Fundacao de Ciencia e Tecnologia), a State Institute of applied research and engineering, and was host to several Industrial Associations as well as technicians belonging to specific fields:

   - chemical and pharmaceutic industries;
   - leather and shoe industry;
   - cellulose and paper industries;
   - fertilizer industry.

   The presence of about 230 technicians from various industries at this meeting shows the great interest of this subject in Brazil.

   The Project was requested to participate with some lectures on solid wastes from leather industry. A technician of the Italian Staff at that moment present in the Project area together with a member of the Brazilian Team delivered two lectures concerning "The final disposal and the possible utilization of tannery sludge" (Mr. Piero NINI) and "The chemical conditioning of primary treatment tannery sludge" (Mr. Jose Luiz MERIGO).

   The relevant part of Mr. NINI's lecture is reported in this paper (see paragraph 3.2 "Disposal of tannery solid wastes").

b. On July 1986 together with Mr. Paulo JOST (Project National Coordinator) and Mr. Hugo SPRINGER (Director of SENAI School at Estancia Velha), the Italian Team Leader took part in a meeting in São Paulo organized by the Leather Industry Association of this State. In this meeting, the aims and the activities of UNIDO/SENAI Project were illustrated.

c. From 14 to 15 November 1986 a short course (Seminario Sobre Tratamento de Efluentes du Curtume) was held by the Italian Team leader at the SENAI School of Water Control and Protection, Curitiba (Paranà). Seventeen persons took part in this course:

- technicians of local tanneries (Adriatico and Curitiba);
- technicians of SUREMA (Superintendencia de Recursos Hidricos e Meio Ambiente do Paranà);
- technicians of SANEPAR (Companhia de Abastecimento de Agua e Saneamento Basico do Paranà).

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6. CONCLUSION AND FINAL OBSERVATIONS

We believe that the objectives of the Project have been achieved and that we have fulfilled our assignment.

- The pilot plant and the installed eqipment have demonstrated their reliability at the same European level under local conditions in the treatment of tannery effluents; furthermore, the secondary units show better performances for climatic reasons. This pilot plant was necessary to train local consulting engineers able to design adequate projects and to facilitate the tanners' choice of the most suitable solutions.
  In addition many local constructors have visited and studied the pilot plant. Equipment formerly unavailable in Brazil is now locally produced.
- The training of Brazilian personnel is finished. They are able to support the Project "inheritance" and to continue and improve the technical assistance to the leather industry.
- The new laboratory of the Project (inaugurated on March 1986) is fully operative and able to make all the most important analyses of effluents and solid wastes.
  This important service is more and more requested by tanners of Rio Grande do Sul; in the near future it will be increased at the same rate of plants installation.
- The totality of Brazilian tanneries and allied industries know the Project, and a relevant part of them have already utilized the Project services.

With the expiration of the UNIDO Project US/BRA/80/166, the SENAI School of Estancia Velha has taken entirely in its hands the management of the Brazilian Team, the pilot plant and the laboratory.

Now the SENAI Counterpart must continue the Project activities and be prepared for the moment when all the projected plants will be installed and put in operation.
In the next future the number of technicians involved in this activity must be adequate to the tanners' demand for assistance (the availability of personnel is now inadequate). Furthermore the activity must not be limited to the tannery industry of Rio Grande do Sul but continued in the other Brazilian States and extended throughout Latin America.

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A N N E X E S

I - Contractual Duties

II - Ultrafiltration Process

III - Flotation Process

IV - Microbiology Applied to the Treatment of Tannery Effluents

V - Geology Applied to Solid Wastes Disposal

VI - List of Visited Factories

VII - Tannery Alianca S.A. Project

ANNEX I

Contractual duties

The aim of this Contract is to establish a pilot demonstration plant for tannery effluents treatment capable of:

- assisting the Brazilian tanning and allied industries to obtain a reduction in the levels of pollutants of their effluents and to achieve the norms established by the competent authorities;
- assisting both the local authorities and the tanning industry in the preparation and evaluation of the technically feasible projects necessary to achieve such lower pollution at low economical cost;
- evaluating, under local conditions, the effectiveness of a variety of effluents treatment techniques;
- conducting a systematic programme of training to develop a cadre of qualified personnel in this field;
- carrying out a programme of applied research in the treatment of tannery wastes and the economic recovery of materials from such wastes;
- preparing major outlines of the most suitable system to be applied in individual tanneries and joint municipal effluent treatment plants in Brazil, and
- preparing recommendations on how better dispose of/utilize the tannery sludges and other solid wastes.

Contractor's service

For the performances of his obligations under this Contract, the Contractor shall make available a total of ten point five (10.5) man/months of personnel services as specified in sub-paragraphs a) and b) immediately hereafter.

a) Project area services

Nine (9) man/months of service shall be carried out in the Project area.

b) Home office services

One point five (1.5) man/months of service shall be carried out at the Contractor's Home Office.

Name, function and duration of the assignment of the Contractor's personnel

The personnel provided by the Contractor and the duration of their assignment were as follow:

Name	Function	Duration of assignment (m/m) Project area	Home Office
Mr. G. Clonfero	Chemist	4.0	altogether 1.5
Mr. P. Nini	Chemist	2.9	
Mr. G. Franci	Geologist	1.4	
Mr. M. Bacchi	Biologist	0.7	
Total		**9.0**	**1.5**
Grand total		**10.5**	

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ANNEX II

Ultrafiltration process

Ultrafiltration (UF) is a name given to a form of suspended solids separation which employs relatively coarse membranes at relatively low pressures. The process should be distinguished from reverse osmosis, which is a similar process used for dissolved solids separation using fine membranes and high pressures. Ultrafiltration, using a thin semipermeable polymeric membrane, is reported most successful in separating suspended solids as well as large-molecule colloidal solids (0.002 to 10.0 µm) from waste water.

Fluid transport and solids retention are achieved by regulating the pore-size openings. Thus, the ultrafiltration process is a physical screening through molecular-sized openings rather than one controlled by molecular diffusion.

The size of the pores determines the cut-off, that is to say the minimum diameter of the retainable particles. Really the effective filtering layer is made, in addition to the membrane, by the limit layer which develops on the membrane itself as the plant runs.

By ultrafiltration is possible to separate from the solvent colloids or macromolecules with a molecular weight between 1,000 and 100,000; the permeate flow varies between 500 and 5,000 l/m^2 of membrane per day.

In a UF system (see fig. 1), a feed water is introduced into a membrane module. Water and low molecular weight solutes, passes through the membrane and are removed as permeate. Suspended solids, and high molecular weight species are rejected by the membrane and are removed as concentrate.

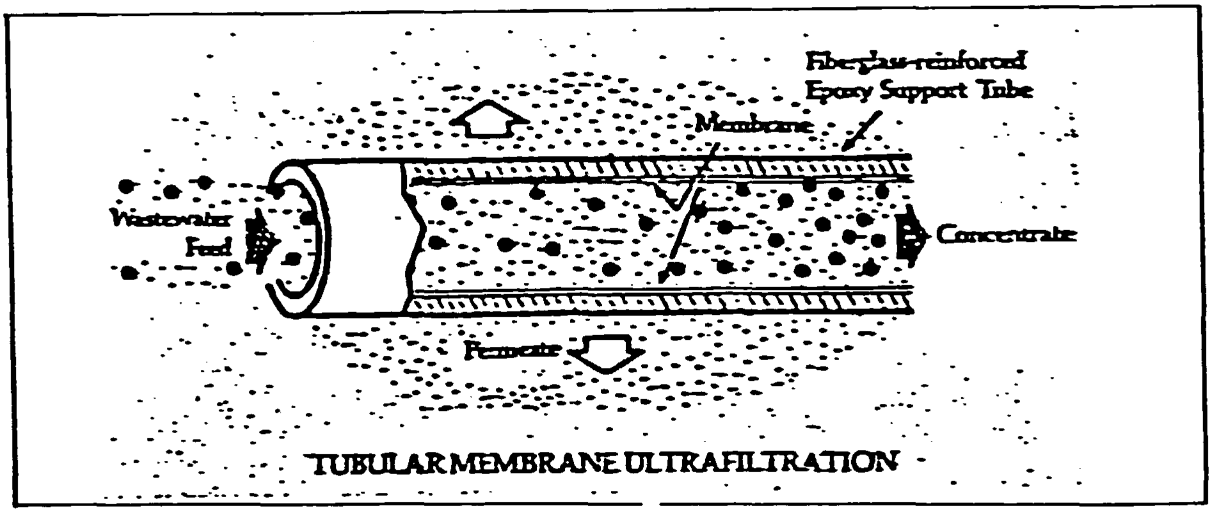

figure 1

In ultrafiltration, the feed stream flows across the membrane surface. This characteristic cross-flow differs from the perpendicular flow of ordinary filtration. In ordinary filtration a filter cake builds up on filter surface and requires frequent filter replacement or cleaning. In ultrafiltration cross flow prevents filter cake buildup, and high filtration rates can be mantained continuously.

Membrane description

Ultrafiltration membranes are thin films of proprietary non-cellulosic polymers. The most utilized polymers are poly-sulphonated and polyamides, which show high chemical, mechanical and thermic resistances.
The poly-sulphonate membranes, employed in the recovery of sulphide from spent lime baths, are able to work in a range of pH from 1 to 14 and can resist to a 2% Sodium Hypochlorite or 10% Hydrogen Peroxide solutions and to a temperature up to 100°C.
Water permeability is utilized to characterize the porosity

of the membrane, but does not represent the stabilized, long-term flux on a process fluid. In the waste treatment field, fluxes of 15 to 20 l/m^2 of membrane surface per hour are typical.

Membrane life is a function of fouling and required flux rates. E.P.A. standards indicate that a membrane may be considered acceptable for a life span of 6 months in continuous operation with a minimum initial flux of 30 and a final flux of 15 l/m^2 per hour. A plant must be designed for the lower figure and the membrane replacement made when the design figure is reached.

The driving force for transport of water through the membrane is pressure. Operation is achieved at pressure gradients of approximately 2 bars. Total system pressures do not exceed 5 bars.

Ultrafiltration modules

The ultrafiltration membranes may be assembled in several manners. This aspect of design concerns the amount of membrane surface area which can be incorporated into a module. Because of low membrane fluxes,it is imperative to design the module to maximize membrane surface area.

- Tubular: diffusely employed, especially when the suspended solids are high - prefiltration not always necessary - easy regeneration - quick replacement of the membranes;
- multitubular: high flow of permeate - with the same permeate flow, the energy requirement of the multitubular type is lower than that of the first type;
- spiral: employed with low content of suspended solids - high performances and low energy requirement - high operative pressure and temperature;

- capillary: employed both for liquids and for gases - minimum energy requirement - careful prefiltration required.

Working parameters

The best working parameters will be stated everytime considering:

a. type of membranes;

b. feed characteristics;

c. circulation flow (i.e. tangential velocity of the feed in the modules);

d. differential pressure of the liquid on the two surfaces of the membrane;

e. eventual pretreatments;

f. eventual recovery process of substances from concentrate.

The parameters which characterize the membranes are:

- retention: is the per cent of solute which does not pass through the membrane:

$$\text{retention of solute X} = \frac{[X]_{feed} - [X]_{permeate}}{[X]_{feed}} \times 100$$

- yeld: is the per cent of a solute recovered in the concentrate:

$$\text{yeld} = \frac{\text{total quantity of solute in the concentrate}}{\text{total quantity of solute in the feed}} \times 100$$

- specific flow: is the volume of permeate which passes through the unit surface in the unit of time: l/m^2 of membrane per hour. Furthermore, the flow of permeate depends on the liquor temperature, the working pressure, and the final concentration of the feed requested.

- Water flux determination: water flux is the rate of permeation measured by circulating clean water through the ultrafilter. Determining this rate will give an indication of the cleanliness of the membrane surface and effectiveness of the cleaning procedure.
- Standard conditions and corrections: standard conditions for measuring flow are set at an average pressure of 3.5 bars and a temperature of 25°C. Because these conditions are not optimum on clean water, the measured flow must be corrected for temperature and pressure. Water flux should be taken with an inlet pressure of 1.5 bars due to the high rate of permeation exhibited by clean water.

  The units for water flux are litres of permeate per square meters of membrane per hour.

$$J_m = \frac{\text{average permeate rate in liters/hour}}{\text{total membrane area in sq. meters}}$$

J_m = measured flow

The measured flow, can be corrected to standard conditions using the following equation:

$$J_{corr} = \frac{J_m \times 6.8}{P_{in} + P_{out}} \times F$$

where:

. P_{in} = inlet pressure;

. P_{out} = outlet pressure;

. F = temperature correction factor (see table I);

. 6.8 = constant factor.

table I : temperature correction factor

T(°C)	F	T(°C)	F
53	0.595	28	0.935
51	0.605	27	0.956
50	0.615	26	0.978
49	0.625	25	1.000
48	0.636	24	1.023
47	0.647	23	1.047
46	0.658	22	1.072
45	0.670	21	1.098
44	0.682	20	1.125
43	0.694	19	1.152
42	0.707	18	1.181
41	0.720	17	1.212
40	0.734	16	1.243
39	0.748	15	1.276
38	0.762	14	1.310
37	0.777	13	1.346
36	0.793		1.383
35	0.808		1.422
34	0.825	10	1.463
33	0.842	9	1.506
32	0.859	8	1.551
31	0.877	7	1.598
30	0.896	6	1.648
29	0.915	5	1.699

Applications of ultrafiltration in tannery

Ultrafiltration is not widely adopted at the present in tannery because of its high cost and operative complexity.

The possible applications in tannery are:

a. spent unhairing baths recycle (see fig. 2)

A high portion (40-70%) of the total BOD_5 and COD of a tannery waste water is related to the spent unhairing baths; by means of the ultrafiltration it is possible to separate and concentrate a large part of this polluting load and, at the same time, to recover and reuse the residual sulphide. For this use the membranes are generally assembled in the tubular manner.

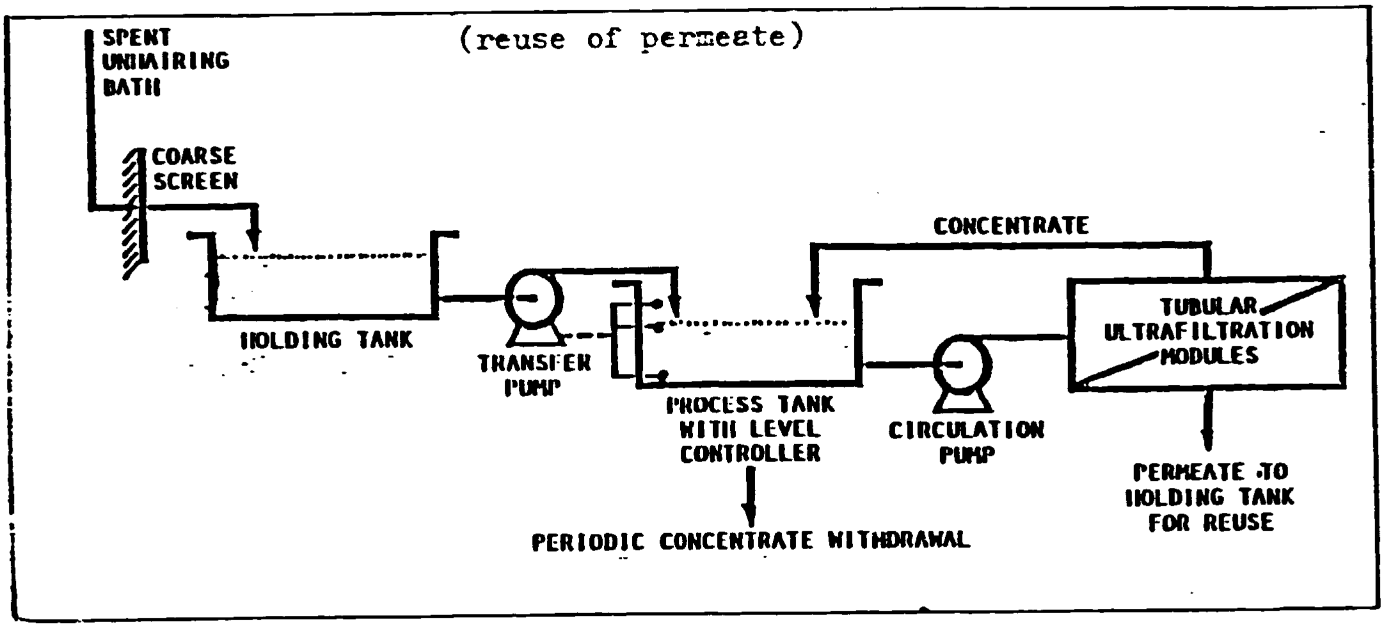

figure 2

b. Recovery of tannin from spent vegetable tannin light liquor (see fig. 3)

The spent vegetable tan liquor is filtered in order to increase the tannin non tannin ratio in the concentrate which can be reused after the treatment as fresh vegetable tan liquor, in fact, unlike in the unhairing bath application the concentrate and not the permeate is reused.

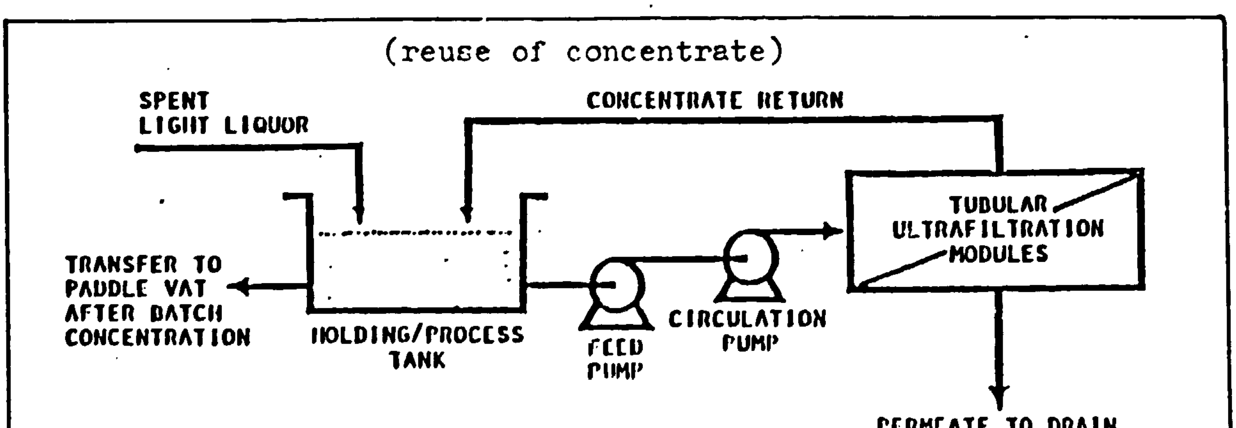

figure 3

c. Other possible applications

Two possible applications of ultrafiltration are presently being experimented. The first is the removal of grease and chemicals (surfactants and solvents) and recycling of brine from spent baths of goat and sheepskin degreasing. The second is the chrome recovery, after flocculation, from spent tanning liquors; the chrome recovered from the concentrate after acidification can be employed again for tannage and the permeate discharged or employed to prepare the pickle.

References

1. Process design manual for suspended solids removal. U.S. E.P.A. - Washington , 1975.
2. Myles H. Kleper: "A new approach for treatment of spent tannery liquors". Memory lecture presented at the American Leather Chemists Association - 75th Annual Meeting, 1979.

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ANNEX III

Flotation process

Flotation is a clarification and/or thickening process similar to gravity sedimentation, but one in which the solids float to the surface of the water, where they are skimmed off, instead of settling to the bottom where they are scraped to a point for removal by gravity or pumping. Obviously, a floating particle must have a specific gravity less than that of water.

Such substances have such a low specific gravity in their natural form (such as oils, greases, some plastics etc.); they will float to the surface on their own (autoflotation). In most case, however, particles which are naturally heavier than water are made lighter by attaching many small air bubbles to them so that the specific gravity of the particles-bubble combination is less than that of water (air flotation). The bubbles may be added to the waste water by entrapping air in the liquid by aeration (diffused air flotation), or by suddenly reducing the pressure on a supersaturated portion of the waste, causing the excess of air to come out of solution as bubbles (dissolved air flotation). Since the second method produces much finer bubbles (50-100 μm vs 500-1,000 μm), which adere to the waste particles much better, it is preferred in most cases.

In comparison with gravity sedimentation, flotation shows the following advantages:

- higher hydraulic loadings, hence smaller tank size with shorter retention time;
- effectiveness in removing fine suspended solids which are difficult to settle, hence improvement in the quality of

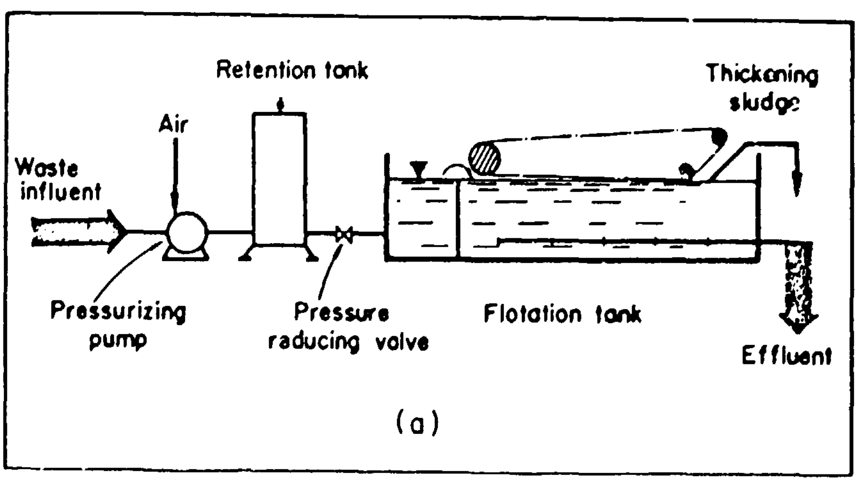
the effluent;

- higher solids content of the floated sludges.

Dissolved air flotation (DAF)

In the simplest form of dissolved air flotation, shown schematically in fig. 1, the waste water is pressurized to a pressure of 2 to 5 bars in a small solution tank of about 1 min detention time. The air may be aspirated into the suction side of the pump or pressurized air may be injected directly into the solution tank. Since the solubility of a gas in water is proportional to the pressure of the gas, 4 times as much air can be dissolved in water at the pressure of 4 bars as at a normal pressure of 1 bar. When the pressure of the solution is suddenly reduced as the waste is injected in the flotation tank through a pressure reducing valve, the saturation concentration of air is also reduced and the excess of air in solution tends to come out of solution as tiny bubbles. The bubbles tend to form readily at phase interfaces, such as the surface of particles, and especially at sharp angles in the interfaces making the particles to float. Coagulants, such as aluminium or iron salts, or high molecular weight organic polyelectrolytes, are commonly used just in sedimentation and are very effective in many cases.

figure 1 from (1)



There is a maximum amount of air, or number of bubbles, that can be effectively absorbed or entrapped in a given waste or sludge. The optimum amount of air is directly proportional to the solids content of the waste or sludge. Thus the air/solids ratio (A/S ratio) is the critical design variable. Expressed as weight of air released from solution per weight of solids in the influent, it directly affects all three measures of performances of a flotation unit, which are:

- the solid content or thickness of the float;
- the suspended solids content of the effluent;
- the ascension speed of the float, which determines the overflow rate necessary, and the size of basin required.

Each of these three variables is improved by an increase in air/solids ratio up to a point which is different for each waste. The air/solids ratio is:

$$A/S = \frac{C_s \left[f \ (P + 1) - 1 \right]}{X_a} \qquad (a)$$

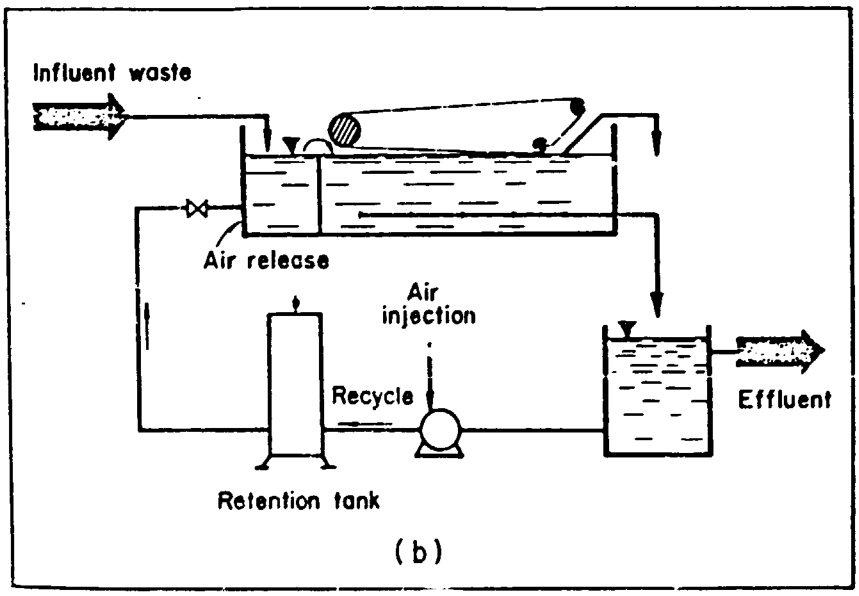
where:

- A/S = air/solids ratio;
- C_s = concentration of air in water at the saturation at the temperature of water (mg/l);
- P = pressure in the solution tank (bars);
- X_a = influent suspended solids concentration (mg/l);
- f = constant linked with the efficiency of the solution tank (generally 0.5).

Since the quantity of air which can be dissolved in a certain volume of influent is limited, it is possible that, when the influent suspended solids concentration exceeds

1,000-1,500 mg/l, the maximum values of A/S ratio obtainable are too low to allow complete flotation. In these cases, part of the effluent is recycled and mixed with the influent in order to obtain a dilution effect which determines an increasing of the A/S ratio.
Furthermore, some wastes or sludges, which either consist of large or stringy organic particles or which are already flocculated, such as waste activated sludges, would be sheared into smaller particles by the action of the pressurizing pump. In these cases a portion of the clarified effluent is pressurized and injected into the waste water or sludge line leading to the flotation unit or into the flotation unit just below the waste water or sludge influent line.
This system is shown in fig. 2.

figure 2 - from (1)



When the recycled flow is pressurized, the equation (a) becomes:

$$A/S = \frac{R\,C_s\left[f\cdot(P+1)-1\right]}{Q\,X_a} \qquad (b)$$

where:

- R = total flow to the unit (influent + recycle);
- Q = influent flow rate.

Typical values of A/S ratio are 0.02 to 0.06 and are varied in practice by varying the pressure, recycle ratio and detention time in the solution tank. Typical values cited are reported in table I.

table I – from (3) modified

Parameter	Range
Pressure, bars	2 to 5
Air to Solids Ratio, kg/kg	0.02 to 0.06
Float Detention Time, min.	20 to 60
Surface Hydraulic Loading, m^3/m^2h	0.5 to 0.7
Recycle, percent	up to 120

References

(1) Thackston, E., W.W. Eckenfelder (edited by): Process Design in Water Quality Engineering - Jenkins, 1972.

(2) Eckenfelder, W.W. (edited by): Industrial Water Pollution Control - Mc Graw-Hill, 1972.

(3) U.S. Environmental Protection Agency : Suspended Solids Removal - E.P.A. 625/1-75-003, 1975.

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ANNEX IV

Microbiology applied to the treatment of tannery effluents

Studies on the metabolism, biochemistry and physiology of microorganisms, in particular Bacteria, are obviously important in used-water treatment systems' planning and management because understanding of the microbiological mechanisms involved helps to improve the efficiency of the processes. It is important to realize that all microbial systems c e on the same general principles, and that the differences between the various biological systems lie in the environment imposed by the mechanical aspect of the system.

Program of the course

a. Short survey of biochemistry

Given the university formation of the Brazilian Technician (Chemical Engineers and not Biologists) it was deemed useful to make a short survey on the following arguments:

- amino acids and prot ins;
- enzymes;
- fats;
- carbohydrates;
- nucleotides essential in metabolic reactions.

b. The Bacteria

Bacteria are the most important group of organisms living in a biological treatment system. They play an essential role in removi..g the organic matter. For this reason the course dealt widely with Bacteria and, particularly, with those aspects of Bacteriology directly connected with the biological treatments in tannery.

The principal components of a bacterial cell were briefly described together with some physiological aspects connected with the operation of a biological treatment:

- growth phase;
- bio-flocculation;
- nutritional requirements;
- effects of some toxic substances present in tannery effluents (e.g. Chrome III, Sulphides, Ammonia Nitrogen, Phenols etc.)

Furthermore, particular emphasis was given to two arguments directly connected with the correct operation of a biological treatment system:

- **slime layer:** is the outermost layer of the Bacteria. It is an accumulation of polysaccharides around the cell and appears to be a degradation product of the cell wall. This layer is very important in the biological processes; in fact, the sludge floc of an activated sludge or the bio-film of a percolating filter are constituted by Bacteria embedded in a common gelatinous matrix made by the slime layers of the single cells. Therefore, the formation of slime layer is the most important step in the development of activated sludge because it allows the flocculation of the cells, which may be retained in the system as sludge flocs. Observing a fixed and stained (methylene blue or gentian violet), or a fresh smear of activated sludge, it is possible, within certain limits, to obtain information on the "status" of a plant.

So, as practical test, several slides were prepared utilizing the mixed liquor from the oxidation ditch and read on the basis of the method of Drakides (6). This method, which allows to correlate the microscopic characteristics of the sludge (slime layer, floc structure etc.) to the efficiency of the plant, is, on the ground of our experience, applicable also to the biolcgical sludge of tannery.

From this analysis the oxidation ditch mixed liquor resulted young and heavily loaded: a confirmation tnat in those days a large quantity of excess sludge was discharged.

- **Identification of bulking organisms.** Bulking, a condition in which the sludge does not settle well and has low densities (or high SVI - sludge volume index), presents serious trouble in secondary sedimentation and effluents with high concentration of suspended solids. Bulking in tannery waste water treatment may depend on a variety of causes, the most common of which are:
  - filamentous bulking: caused by filamentous organisms like Zoophagus and Sphaerotilus (Fungi) or Thiothrix and Beggiatoa (Bacteria). Fungi may overcome aerobic Bacteria for the following reasons:
    . low pH of the liquor;
    . high BOD:P and/or BOD:N ratios;
    . overload shocks;
    . toxic substances shocks;
    . low dissolved oxygen levels.

Furthermore, the presence of H_2S in high concentration, frequent in tannery waste water, may encourage filamentous sulphur Bacteria like Beggiatoa and Thiothrix.

  - Zoogleal bulking: caused by the presence of excess exocellular hydrophilic polysaccharides (slime layer) produced by several species of Bacteria (e.g. Zooglea ramigera). Thus, although it is indispensable to promote good settling, excess of such substances is likely to cause bulking.

The main groups of bulking organisms in tannery waste water were identified using slides prepared with the sludge of the oxidation ditch. The possible interventions to eliminate or prevent bulking (e.g. control of BOD:P and BOD:N ratios, control of H_2S, use of Chlorine or H_2O_2, increasing the biological sludge wastage) were explained.

c. The metabolism

Since the Bacteria are the most important organisms, the course dealt particularly with their metabolism. It described the reactions of organic matter degradation both in aerobic and anaerobic conditions, together with those particular metabolic cycles typical of Bacteria (e.g. Sulphur Bacteria) present in tannery plants. The subjects treated are listed below:

- metabolism: anabolism and katabolism;
- autotrophic and eterotrophic Bacteria;
- aerobic, anaerobic and facultative Bacteria;
- degradation of proteins, fats and polysaccharides both in aerobic and anaerobic conditions. Particular attention was given to the metabolism of those substances which are most common in tannery waste water, e.g. fibrous proteins (keratins, collagen) and fats;
- nitrogen cycle: nitrification, denitrification etc.;
- sulphur cycle: Sulphur bacteria reactions.

d. The Protozoa present in tannery activated sludge plants: their role and significance as indicator organisms

This part of the course treated the microscope as an analytical tool for the control of tannery-activated sludge plants. The Protozoa commonly observed in the mixed liquor may be considered important for two reasons: first, they accomplish an important "cleaning" of the effluent; in fact their predatory activity drives to the removal of the majority of dispersed Bacteria and so improves the effluent quality. (see fig. 1 from 4)

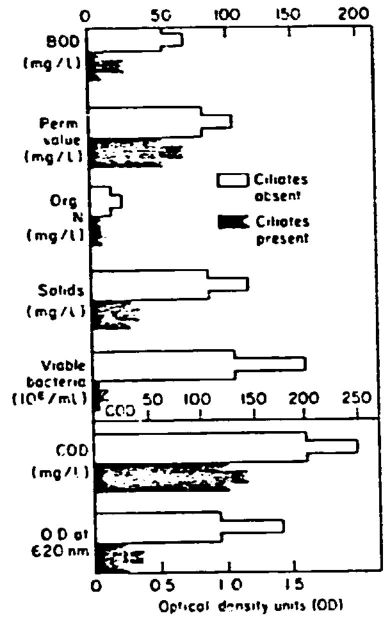

FIG. 1 Histogram of effluent qualities from experimental activated-sludge units operating in absence and presence of ciliated protozoa Shoulders on blocks indicate ranges of means of effluent quality.

Second, since the activated sludge plants are a habitat in which (as in natural ecosystems) the various species are linked each other by complex ecological relationships, whatever produces a change at any point of the ecological chain influences tha entire living community.

The microorganisms follw precise ecological patterns in every activated sludge system; they respond to chemical changes in the habitat (e.g. D O , toxic substances, sludge age etc.) by alterations in the number of organisms belonging to each species. So it is possible to define the operating characteristics of a plant by routine microscopic examination of the mixed liquor. Protozoa, easily visible with a microscope, are the best objects for such investigations.

During the course the analytical method for the examination of an activated sludge was described and shown in laboratory. The number of Protozoa were evaluated, the main groups as well as the dominating species were identified.

The interpretation of these results permitted us to quickly assess the "state of health" of a plant.

Furthermore, during the practical activity, some theoretical lessons were given on the following arguments:

- ecology of biological treatment plants;
- groups of Protozoa and their characteristics;
- identification of the species commonly present in tannery activated sludge and their significance as indicator organisms.

References

At the beginning of the course, a series of specific technical papers on the treated arguments and a summary of Biochemistry were given to the participants.

(1) Lehninger, A.L. : "Biochemistry", New York, Worth Publisher, 1975.

(2) Pelczar, M.J., R.D. Reid and E.C.S. Chan: "Microbiology" Mc Graw-Hill, 1977.

(3) Mitchell, R.: "Water Pollution Microbiology". Wiley Interscience, 1971.

(4) Curds, C.R. and H.A. Hawkes: "Ecological Aspects of Used Water Treatment". Academic Press, Vol.I,II and III, 1983.

(5) Madoni, P.: "I Protozoi Ciliati negli Impianti Biologici di Depurazione" Italian National Research Council, 1981.

(6) Drakides, C. : "L'observation microscopique de boues activées appliquée à la surveillance des installations d'epuration" T.S.M. L'EAU, 73 85-98, 1978.

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ANNEX V

Geology applied to solid waste disposal

Controlled landfill

Disposal on land is the most common method in use today for the long-term handling of solid wastes and residual sludges. The most common advanced land-disposal system, more and more utilized in industrialized countries, is controlled landfill, that is to say, a disposal site constructed and correctly managed under an ecological point of view. The planning, analysis and design of controlled landfills make use of several scientific and engineering principles.

a. Site selection

Usually are selected deserted mines or quarries to reclaim; gorges, dolinas or areas subjected to inundation or under hydrogeologic ties, are clearly discarded. the site suitable for landfill must answer to such general requisites as distance from inhabited areas but more important must fulfill geologic and hydrogeologic conditions in order to be suitable as a landfill site. In fact, the main ecological risk of landfilling is the possible pollution of ground waters.

The selection of the area is generally subjected to the following analyses:

geologic analyses: their object is to establish the characteristics of the geologic units which constitute the subsoil of the site: thickness, lithology, permeability and porosity. Typical permeability coefficients for various soils are reported as example in table I.

table I : typical permeability coefficients for various soils (laminar flow) - from (1) modified

Material	Coefficient of permeability K_s - $1 / m^2$ per day
Uniform coarse sand	406,700
Uniform medium sand	101,500
Clean, well-graded sand and gravel	101,500
Uniform fine sand	4,080
Well-graded silty sand and gravel	395
Silty sand	89
Uniform silt	48
Sandy clay	4.8
Silty clay	0.89
Clay (30 to 50 percent clay sizes)	0.089
Colloidal clay	0.00089

geotechnical analyses: their object is to learn the mechanical characteristics of the soil by means of penetrometric and other mechanical tests. These tests, undertaken to determine the cohesion and the interior friction angle of a soil, allow us to know the load-limit to which it can be subjected. This data is indispensable for avoiding deformations and soil sinkings which could damage the impermeabilization layer.

hydrogeologic analyses: their object is to establish:

. depth of the water table and its seasonal variations;

. form and direction of the water table and its relations with the superficial waters. Generally zones with deep water table and thick impermeable layers are selected.

b. Sludge characterization

The chemical and mechanical characteristics of the sludge to be disposed directly influence the engineering of landfilling.

The main parameters to evalue are the following:

- solids content of sludge: is related to the nature of waste water treatment and sludge processing steps;
- volatile content: is a measure of the organic content present in the solid fraction of the sludge;
- presence of heavy metals and toxic organic compounds;
- mechanical characteristics: cohesion, porosity, interior friction angle.

Table II reports the values of some parameters relative to the tannery sludges produced by the centralized plants of S. Croce sull'Arno (Pisa) and Ponte a Egola (Pisa).

table II: primary and secondary mixed sludges after 20 days of ageing (°)

	S. Croce - Filterpress -	Ponte a Egola - Band Press -
Solids content: per cent dry solids	30 ÷ 35	24 ÷ 33
Volatile content: per cent by weigh of dry solids	45 ÷ 50	45 ÷ 50
Interior friction angle	16° - 17°	4°
Coefficient of permeability 1/m² per day	1 ÷ 10	0.1 ÷ 10
Load-limit: g/cm²	800	100÷200

(°) Courtesy of Mr. L. Stano - Chief Engineer of TECHNOGEO Pontedera (Pisa)

c. Conventional methods for controlled landfilling

- Digging: the first step in preparing a controlled landfill is to dig the cavity destined to admit the sludges. The removed material, stored, can be later used to cover the sludges.
- Water-proofing of the bottom and the banks of the cavity. If the soil is sufficiently impermeable, the bottom is dig so as to form a slope which allow the waters to flow in the desidered direction.
  If the soil is insufficiently waterproofed, it will be necessary to construct barriers of sealant materials.
  The most common sealants are reported in table III.

table III: landfill sealants for the control of gas and leachate movement (1)

Sealant		
Classification	Representative types	Remarks
Compacted soil		Should contain some clay or fine silt
Compacted clay	Bentonites, illites, kaolinites	Most commonly used sealant for landfills; layer thickness varies from 6 to 48 in; layer must be continuous and not allowed to dry out and crack
Inorganic chemicals	Sodium carbonate, silicate, or pyrosphosphate	Use depends on local soil characteristics
Synthetic chemicals	Polymers, rubber latex	Experimental, use not well established
Synthetic membrane liners	Polyvinyl chloride, butyl rubber, hypalon, polyethylene, nylon-reinforced liners	Expensive, maybe justified where gas is to be recovered
Asphalt	Modified asphalt, rubber-impregnated asphalt, asphalt-covered polypropylene fabric, asphalt concrete	Layer must be thick enough to maintain continuity under differential setting conditions
Others	Gunite concrete, soil cement, plastic soil cement	

- Drainage. To eliminate the leachates, rain water and water released by the sludge, drainage channels are placed at the bottom of the excavation. Constituted by trenches filled with coarse gravel, they converge to drainage shafts where the leachates are collected and pumped to a treatment plant. When a digging, or part of it, is filled, the surface is covered with a layer of clay sloped to avoid rain infiltration.

- Gas control: an important problem in landfilling is connected to the organic biodegradable components which begin to undergo bacterial decomposition as soon they are placed in landfill and give rise to such various gases as ammonia, carbon dioxide, carbon monoxide, hydrogen sulphide, methane. The usual way of removing these gases is to install vent pipes in the sludge mass, at regular distances.
- Ground waters control: a controlled landfill requires periodical control of the ground waters by means of a system of monitoring weels. These are placed all around the landfill site to certify the efficiency of the impermeabilization layer.

  note: the word ground waters means the waters flowing in the subsoil. These waters derive principally from rain which permeates the soil impregnating it to a level called water table. Below this level (saturation zone) the waters are ground waters.

References

(1) G. Tchobanoglous, H. Theisen, R. Eliassen : Solid Waste - Engineering principles and management issues. Mc Graw-Hill, New York, 1977.

(2) Brunner, D.R. and D.J. Keller: Sanitary Landfill Design and Operation. U.S. E.P.A. SW-65ts, Washington, 1972.

(6) E.P.A. : Process Design Manual: Sludge Treatment and Disposal. U.S. E.P.A., publication 625/1-79-011, Cincinnati OH, 1979.

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ANNEX VI

LIST OF VISITED FACTORIES

RIO GRANDE DO SUL

1.	Curtume Rimus SA,Estancia Velha	Modification of primary project and secondary
2.	Calçados Relim SA,Estancia Velha	Centralized plant at E.V. feasibility study
3.	Curtume Matiz SA,Estancia Velha	Modification of primary project
4.	Curtume Schuck SA,Estancia Velha	Modification of primary project and secondary
5.	Curtume Bender SA,Estancia Velha	Modification of primary project and secondary
6.	Curtume Leuck Mattes SA,Estancia Velha	Modification of primary project and secondary
7.	Curtume Berghan LTDA,Estancia Velha	Centralized plant at E.V. feasibility study
8.	Vemaso Industrial de Cuoros LTDA, Estancia Velha	Primary treatment project
9.	Curtume Reinaldo Konrath LTDA, Estancia Velha	Centralized plant at E.V. feasibility study
10.	Curtume Irmâos Slengler e CIA LTDA,Estancia Velha	Centralized plant at E.V. feasibility study
11.	Curtume Estancia LTDA,Estancia Velha	Primary treatment project
12.	Genuino Ind.e Comm.SA,Estancia Velha	Centralized plant at E.V. feesibility study
13.	Finilux SA,Estancia Velha	Centralized plant at E.V. feasibility study
14.	Imbragel Ind.Brasilera Gelatinas e Derivatos LTDA,Estancia Velha	Centralized plant at E.V. feasibility study
15.	Curtume Heeman SA,Erechim	Modification of primary project
16.	Curtume Boa Vista,Portâo	Modification of primary project and secondary
17.	Curtume Buffalo SA,Portâo	Primary treatment project
18.	Curtume Integral LTDA,Portâo	Modification of primary project and secondary
19.	Curtume A.P.Muller e Cia LTDA,Portâo	Modification of primary project and secondary
20.	Curtume Aliança LTDA,Portâo	Modification of primary project

21. Curtume Musa SA, Portão	Primary treatment project
22. Curtume Kern Mattes SA, Portão	Primary treatment project
23. Curtume Winck Ely e CIA LTDA, Portão	Modification of primary project
24. Curtume Marchini SA, Novo Hamburgo	Modification of primary project
25. Curtume A.Jaeger e CIA LTDA, Novo Hamburgo	Primary and secondary treatment project
26. Curtume Bier Scharlau SA, São Leopoldo	Modification of primary project
27. Curtume Pelesinos LTDA, São Leopoldo	Modification of primary treatment
28. Curtume A.Buhler SA, Ivoti	Modification of primary treatment
29. Ind.de Peles Minuano SA, Ivoti	Secondary treatment project
30. Curtume Fasolo SA, Bento Gonçalves	Modification of primary project and secondary
31. Frango Sul Agro Avicola Industrial LTDA, Montenegro	Secondary treatment project
32. Curtume Marauense SA, Marau	Modification of primary treatment and secondary project
33. Curtume Hummes SA, Salvador do Sul	Modification of primary project
34. Curtume Galvano Miola SA, Erechim	Modification of primary project
35. Frigorifico Zucchetti SA, Nova Araçâ	Secondary treatment project
36. Pincéis Alvorada SA, Alvorada	Modification of primary project
37. Curtume Eré SA, Getulio Vargas	Modification of primary treatment
38. Irmâos Frizzo e CIA LTDA, Jaguerì	Primary and secondary project
39. Curtume Ritter SA, Nova Petropolis	Modification of primary treatment
40. Curtume Monbelli e CIA, Tapera	Modification of primary treatment
41. Curtume Galeazzi SA, Veranopolis	Modification of primary treatment
42. Curtume Closs SA	Modification of primary treatment
43. Curtume Sander LTDA	Primary operational assistance
44. Curtume Eldorado SA	Outline primary project
45. Curtume Ciplame SA, Passo Fundo	Modification of primary project
46. Curtume Becol SA, Novo Hamburgo	Primary and secondary project

OTHER STATES

1.	Curtume Cobrasil LTDA,Parnaiba (Piaui)	Modification of primary treatment and secondary project + assistance in oparational phase
2.	Curtume Recamonde & CIA,Fortaleza (Cearà)	Primary & secondary treatment outline and Chome & Sulphide recycle project
3.	Grandes Curtumes Cearenses SA, Fortaleza (Cearà)	Primary treatment project and chrome & sulphide recycle
4.	Curcel Curtido do Cearà,Paiuçara (Cearà)	Primary treatment project evaluation + screens and ox.ditch rotor design
5.	Curtume Aliança SA,Jequié (Bahia)	Primary & secondary treatment project and chrome & sulphide recovery
6.	Curtume Campelo SA, Juazeiro (Bahia)	Primary project and sulphide & chrome recycle
7.	Curtume California SA,Carpina (Fernambuco)	Primary treatment project
8.	Curtume Inpasa SA,João Pessca (Paraiba)	Primary treatment project
9.	Irmâos Coutinho Ind.de Cuoros SA, Caruaru (Pernambuco)	Primary treatment project
10.	Curtume Argos SA,Caruaru (Pernambuco)	Primary treatment project
11.	Curtume Santa Helena SA, Belo Horizonte (Minas Gerais)	Primary treatment project and chrome & sulphide recycle
12.	Curtume Santa Matilde LTDA, Ubà (Minas Gerais)	Primary & secondary treatment project and chrome recycle
13.	Curtume Adriatico SA,Rio Negro (Paranà)	Primary & secondary treatment and chrome & sulphide recycle
14.	Curtume Cortnorte SA,Montes Claros (Minas Gerais)	Modification to primary & secondary(facultative lagoon)treatment
15.	Curtume Krambek SA,Juiz de Fora (Pernambuco)	Primary treatment project
16.	Curtume Monteiro SA,Caruaru (Pernambuco)	Primary treatment project
17.	Curtume Viposa SA,Caçador (Santa Catarina)	Primary & secondary treatment and chrome recycle
18.	Curtume Carioca SA,Penha (Rio de Janeiro)	Evaluation of primary treatment project
19.	Curtume S.Antonio de Floresta, Fortaleza (Cearà)	Primary treatment project
20.	Curtume Campo Grande SA,Campo Grande (Mato Grosso do Sul)	Primary & secondary treatment project and chrome recycle

21.	Curtume Nacional SA,Rio de Janeiro (Rio de Janeiro)	Primary treatment project
22.	Curtume Catanduva SA,Bom Jardim (São Paulo)	Modification of primary project
23.	Curtume Jacobsen SA, Indaial (Santa Catarina)	Primary & secondary treatment project
24.	Curtume Alvorada LTDA,Mogi Mirim (São Paulo)	Modification of primary project
25.	Curtume A.Cantusio SA,Campines (São Paulo)	Modification of primary project
26.	Curtume Firmino Costa SA,Campinas (São Paulo)	Modification of primary project
27.	Curtume Fasolo SA,Fernandopolis (São Paulo)	Modification of primary project and outlines of secondary treatment
28.	J.Motta,Curtume São Francisco SA, Natal (Rio Grande do Norte)	Chrome & sumphide recycle projects and primary project
29.	Curtume Perdigão SA,Perdigão (Minas Gerais)	Modification of primary project
30.	Curtume P[illegible]i SA,Leme (São Paulo)	Technical suggestions on existing plant
31.	Curtume Santa Genoveva SA,Aquai (São Paulo)	Technical suggestions on existing plant
32.	Curtume Curitiba SA,Curitiba (Paranà)	Modification of primary & secondary project
33.	Curtume Impele SA, (Rio Grande do Norte)	Primary treatment project

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ANNEX VII

Tannery : ALIANCA S.A.

Avenida Lions Clube 188
Jequie - Bahia

M/D : Mr.Juan Llansara
Tech.: Mr.L.Felix de Souza Filho

Old tannery,partially modernized,placed in the suburbs of the city of Jequie by the side of river De Contas.

1. PROJECT DATA
   - 700 hides/day(60-70% wet blue,30-40% crust/finished)green and salted
   - mean weight 29 kg/hide i.e. 20,000 kg of hides/day
   - working time from 07.00 to 20.00
   - water usage 40 l/kg (the water supply is the river De Contas)

   Preliminary remarks

   In the State of Bahia well defined discharge standards for tannery effluents do not exist,so the Federal Standards are adopted.
   Since the tannery is placed near a residential area,it is important to avoid bad smells.
   The river De Contas has a variable flow during the year(see table I), so it is impossible to count on effluent dilution;for these reasons it is advisable an high efficiency treatment plant(primary and secondary).

TABLE I - HYDROELECTRIC COMPANY OF SÃO FRANCISCO

Rio de Contas	mean Q = 35.1 m^3/sec	mean wat.lev.= 0.96 m
	min. Q = 0 " "	min. " " = 0.30 m
	max. Q = 3,160 " "	max. " " = 7.75 m
	max. Q = november - april	
	min. Q = may - october	

The area available for the plant is large (15,000 m^2).

2. PLANT DESIGN DATA
   - tannery effluents volume (Q) : 1,000 m^3/day
   - discharge time (t_d) : 13 h/day
   - mean flow (q_m) : 77 m^3/h
   - peak flow (q_p) : q_mx 1.5 = 115 m^3/h (1.5 peak factor adopted)

   Primary treatment

   1.Screening

   - n° 1 self-cleaning brushed screen,holes Ø 3 mm,surface 6 m^2, capacity 120 m^3/h.

2. Equalization and sulphide oxidation

- treatment time 20 h/day (adopted)
- treatment flow (q_t) = Q/20 = 50 m^3/h
- tank volume :
  - . holding volume (V_s) = (q_m - q_t) x t_{d_3} = 351 m^3
  - . homogeneization volume (V_h) : 150 m^3

    note : V_h was adopted in relation to the characteristics of the floating aerator and is able to assure a good equalization since the lime baths are stored and discharged regularly during the day.
  - . total volume (V_t) = V_s + V_h = 500 m^3
- tank size 13x13x3.6 (H) m , H_{water}: 3 m
- mixing power : 30 W/m^3(adopted)
- total required power : 15 kW
  - . installed n°1 14.8 kW floating aerator;
  - . specific installed power :

    29.2 W/m^3 at max level (3 m)
    43.8 " at med level (2 m)
    87.6 " at min level (1 m).
- sulphide oxidation calculations :

  Na_2S utilized for unhairing (3% Na_2S at 60%) = 600 kg/day equal to 150 kg S^{2-}/day pumped to the treatment plant in 13 h ca.

  note:the spent lime bath,stored in a separate tank,is repumpeu during 13 h/day to the equalization tank.The quantity of S^{2-} arriving in the equalization tank is 8 kg S^{2-}/h and the oxygen request is 12 kg O_2/h.

  Sulphide is mainly oxided to thiosulphate :

  $$2\ S^{2-} + 3/2\ O_2 = S_2O_3^{2-}.$$

  - . total O_2 required = 1.5 x 105 = 160 kg/day (we assumed 70% of the employed S^{2-} in the spent bath i.e. 150 x 0.70 = 105 kg S^{2-}/day)
  - . quantity of O_2 supplied by surface aerator (2.0 kg/kW) = 30 kg/h; the O_2 supplied is able to oxidize the arriving S^{2-} also if a sulphide recycle will not be utilized .

The sulphide oxidation will be catalyzed by Mn^{2+} added as $MnSO_4$ in the equalization tank :

- quantity of Mn^{2+} required : 0.1 kg Mn^{2+}/kg S^{2-} (adopted)
- total Mn^{2+} = 0.1 x 105 = 10.5 kg Mn^{2+}/day i.e. 30÷35 kg of $MnSO_4$ (commercial product)
- $MnSO_4$ solution and dosing unit :
  - . n°1 tank volume 1,000 l ,with electric stirrer 0.74 kW
  - . n°1 dosing pump capacity 30 l/h.

note: if a 10% solution of $MnSO_4$ is utilized, the volume of solution to be dosed is 350 l/day i.e. 30 l/h during 13 h/day.

- lifting :
  n°1 pump capacity 50 m^3/h (adjusted by means of a by-pass).

3. Flocculation

- retention time 3 min (adopted)
- n°1 tank 1.3x1.3x1.7 (H) m (H_{water}: 1.5 m) with slow stirrer (0.4 kW)
- chemicals dosage :
  . Alum 250 mg/l i.e. 250 kg/day of industrial product
  . Polyelectrolyte 1 mg/l i.e. 1 kg/day of anionic powder
- chemicals solution and dosing units :
  . Alum 10% solution i.e. 2,500 l/day
    n°1 fiber-glass reinforced tank volume 3,000 l with electric stirrer (1.5 kW)
    n°1 dosing pump (AISI 316) capacity 0÷250 l/h
  . Polyelectrolyte 0.1% solution i.e. 1,000 l/day
    n°1 fiber-glass reinforced tank volume 1,500 l with electric stirrer (1.1 kW)
    n°1 dosing pump (AISI 304) capacity 0÷100 l/h

4. Sedimentation

- hydraulic surface loading 1 m^3/m^2 per hour (adopted)
- clarifier surface 50 m^2
  . n°1 circular tank Ø 8 m , H_{water}: 2 m , volume 100 m^3 ca., botton slope 10% ca., retention time 2 h ca., sludge scraper (0.3 kW) half bridge installed.

Secondary treatment

- max influent BOD_5 700 mg/l (adopted, after primary)
- organic loading (F) = 700 kg BOD_5/day

Examples of biological treatment alternatives

1. Extended aeration

   - sludge loading (F/M) 0.1 kg BOD_5/kg of suspended solids in the aeration tank per day (adopted)
   - retention time (t) 2 days (adopted)
   - aeration tank volume (V) = 1,000 x 2 = 2,000 m^3
   - total suspended solids (M) 7,000 kg
   - mixed liquor suspended solids (MLSS) 3,500 mg/l

- oxygen requirement (O_r) calculations :

$$O_r = \frac{(a \times F) + (b \times f \times M)}{24} \quad \text{where :}$$

a = O_2/BOD_5 rate : 0.8 kg O_2/kg BOD_5 oxidated (adopted)
F = 700 kg BOD_5/day
b = O_2 rate for sludge endogenous respiration : 0.15 kg O_2/kg MLVSS per day (adopted)
f = MLSS volatile content : 0.8 adopted
M = 7,000 kg
<u>note</u> : MLVSS = mixed liquor volatile suspended solids = MLSS x f

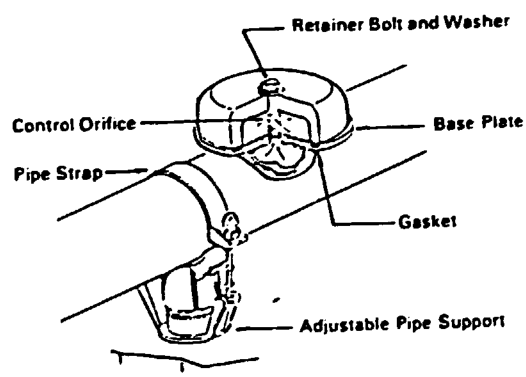
$$O_r = \frac{(0.8 \times 700) + (0.15 \times 0.8 \times 7{,}000)}{24} = 58 \text{ kg } O_2/h$$

<u>Aeration device alternatives</u> :

<u>alternative a/1</u> : dome diffuser (Aluminium oxide, see fig.1)

diameter 17.8 cm
air flow from 0.8 to 4 m^3/h
O_2 transfer efficiency 25÷30%(at standard conditions)

Assumed an air flow of 2 m^3/h per diffuser and an effective O_2 transfer efficiency of 20%, the quantity of O_2 to be furnished is 58 x 100/20 = 290 kg/h i.e. 1,100 Nm^3 of air per hour ca.
- n° of diffusers = 1,100 : 2 = 550



<u>Fig. 1</u>

<u>alternative a/2</u> : plate diffusers (Polyethylene disc, see fig.2)

diameter 21 cm
air flow from 2 to 6 m^3/h (medium size bubbles)
O_2 transfer efficiency 20÷25%(at standard conditions)

Assumed an air flow of 4 m^3/h per diffuser and an effective O_2 transfer efficiency of 15%, the quantity of O_2 to be furnished is 58 x 100/15 = 387 kg/h i.e. 1,400 Nm^3 of air per hour ca.
- n° of diffusers = 1,400 : 4 = 350

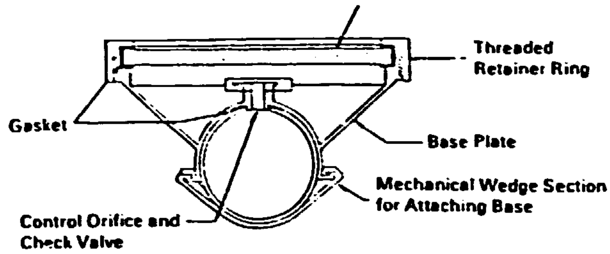


Fig. 2

Air supply device : lobe rotors blower (see fig.3)

- alternative a/1 installed n°2 blowers with the following characteristics (each) :
  capacity 680 Nm^3/h of air
  installed power 14.8 kW
- alternative a/2 installed n°2 blowers with the following characteristics (each) :
  capacity 800 Nm^3/h of air
  installed power 18.5 kW

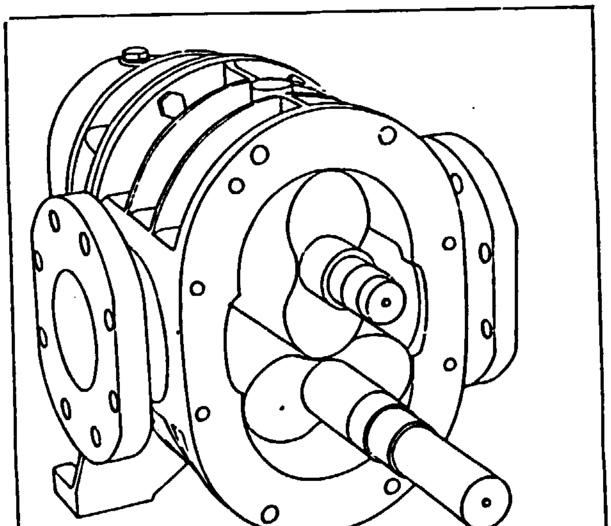


Fig.3

note : O_2 transfer efficiency at standard conditions : the aeration devices suppliers give this datum at 20°C for low salinity waters and fully disareated (DO = 0.0 mg/1).

alternative a/3 : low speed floating aerators(see fig.4)

O_2 transfer capacity 2 kg/kWh

- total necessary power = 58 : 2 = 29 kW

Installed n°2 floating aerators 14.8 kW each.

For geometrical reasons the aeration tank will have the following sizes 17x34x4 (H) m (H_{water}= 3.5 m).

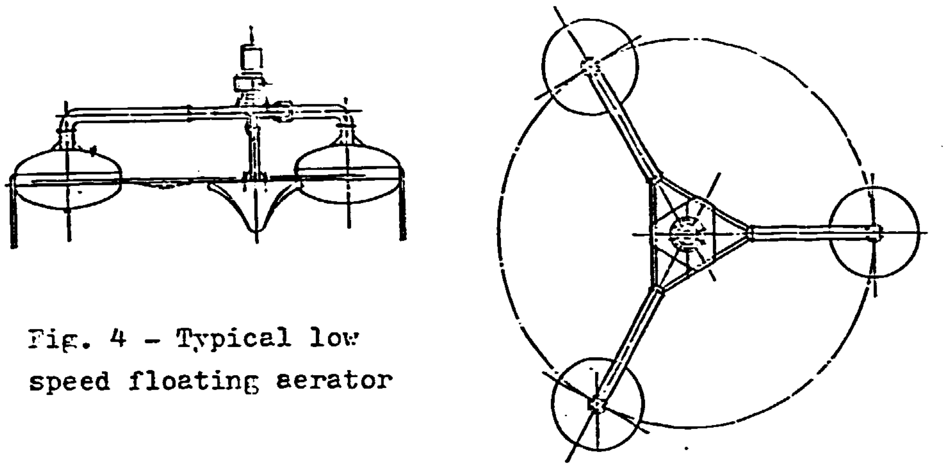


Fig. 4 - Typical low speed floating aerator

alternative a/4 : oxidation rotors (oxidation ditch),see fig.5
diameter 1 m
O_2 transfer efficiency 3 kg/h per metre of rotor at 20 cm immersion
rotors lenght = 58 : 3 = 19.3 m

Installed n°4 rotors with the following characteristics (each)

- lenght 5 m
- installed power 7.5 kW (for a total of 30 kW)

Ditch sizes : two channels 7 m width, H_{water}= 3 m , cross section area 18 m^2 ca , lenght 60 m , volume = 2,000 m^3 ca.

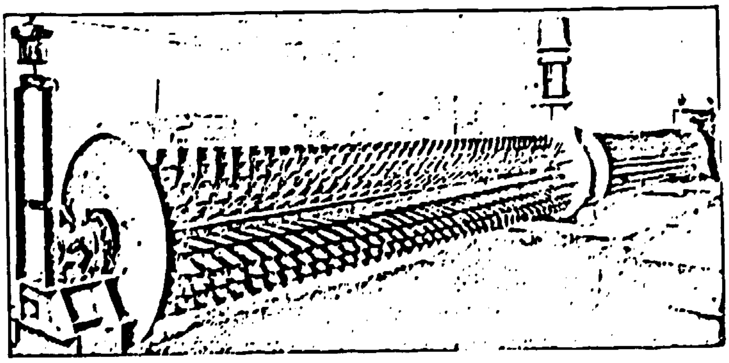


Fig. 5

2. Aerated facultetive lagoon - alternative a/5 -

The dimensioning parameters and procedure reported in section 3.1 of this report are adopted :

- retention time (t) calculation

$$t = \frac{S_o - S_e}{S_e} \times \frac{1}{K_T} \qquad \text{where :}$$

S_o : influent BOD_5 = 700 mg/l
S_e : effluent BOD_5 = 35 mg/l (95% removal efficiency adopted)
K_T : substrate removal rate coefficient = 1.716 $days^{-1}$(see note)

$$t = \frac{(700-35)}{35} \times 1/1.716 = 11 \text{ days}$$

- lagoon volume = 1,000 x 11 = 11,000 m^3
- lagoon depth 2.5 m (adopted)
- lagoon surface = 11,000 : 2.5 = 4,400 m^2
- specific installed power 1.5 W/m^3 (adopted)
- total installed power = 1.5 x 11,000 /1,000 = 16 kW ca
  installed n°4 surface aerators 4 kW each.

note : substrate removal rate coefficient calculation :

$$K_T = K_{20} \times \Theta^{(T-20)} \qquad \text{where :}$$

K_{20} = substrate removal rate coefficient at 20°C = 1.512 $days^{-1}$
Θ = temperature coefficient = 1.016
T = water temperature;since the tannery is placed in the North of Brazil a mean temperature of 28°C has been adopted.

$$K_T = 1.512 \times 1.016^{(28-20)} = 1.716 \text{ days}^{-1}$$

Secondary sedimentation (for alternatives a/1,2,3 and 4)

- hydraulic surface loading 0.5 m^3/m^2 per hour (adopted)
- clarifier surface = 50 : 0.5 = 100 m^2
  installed n°1 circular tank Ø 12 m , H_{water} = 2 m ,volume = 220 m^3, bottom slope 10% ca; n°1 half bridge sludge scraper (0.3 kW) installed.
- retention time = 220 : 50 = 4.4 h

Active sludges recycle (for alternatives a/1,2,3 and 4)

- sludge recycle 100% (adopted)

Installed n°1 centrifugal pump,capacity 30 m^3/h , power 1.5 kW.

SECONDARY TREATMENT ALTERNATIVES: COMPARATIVE TABLE

	Treatment	Tanks costs (sec.sedimentation included for a/1/2/3/4)	Equipment cost (sec.sedimentation included for a/1/2/3/4)	Installed power kW (sludges recycle included for a/1/2/3/4)	Maintenance costs	Area availability m^2
a/1	Ex.aeration with blowers and fine bubbles diffusers	*****	*****	31.4	*****	800
a/2	Ex.aeration with blowers and medium bubbles diffusers	*****	****	38.8	****	800
a/3	Ex.aeration with surface aerators	*****	***	31.4	**	[illegible]
a/4	Ex.aeration with oxidation ditch	****	****	31.8	*	1,000
a/5	Aerated facultative lagoon	*	****	16.0	***	11,000

Sludges treatment

- sludge production factor 0.12 kg (Dry Substance) per kg of processed hide (adopted)
- daily sludge production = 20,000 x 0.12 = 2,400 kg as DS

a. Thickening

- retention time 24 h (adopted)
- surface loading 80 kg DS/m^2 per day (adopted)
- thickener surface = 2,400 : 80 = 30 m^2.

Installed n°1 circular tank Ø 6 m , H_{sludge} = 2.5 m , volume = 70 m^3, bottom slope 25% ca; n°1 full bridge scraper (0.3 kW) installed.

b. Dewatering

alternative b/1 : filter press

- DS of the dewatered sludge 35% (adopted)
- daily volume of the dewatered sludge 6,000 l ca (specific weight 1.2
- n° of filtration cycles 3 per day (adopted)
- filter cake volume = 6,000 : 3 = 2,000 l
  installed n°1 filter with the following characteristics:
  90 plates in polypropilene 1,000 x 1,000 mm
  cake thickness 32 mm
  filtering surface 146 m^2
  filter volume 2,118 l
  working pressure 12 bars
  installed power 3 kW (hydraulic closure and plates displacement).
- feeding pump : installed n°1 piston pump , capacity 5 m^3/h , installed power 4 kW.

alternative b/2 : band press

- DS of the dewatered sludge 25% (adopted)
- n° of working hours 15 per day (adopted)
- equipment capacity = 2,400 : 15 = 160 kg DS/h
  installed n°1 band press with the following characteristics:
  band size 1,000 mm
  capacity 200 kg DS/h
  installed power 1.8 kW
- polyelectrolyte requirement 4 g/kg of DS (adopted)
- daily polyelectrolyte consumption = 4 x 2,400/1,000 = 9,6 kg.
- filter feeding pump:
  installed n°1 helicoidal pump,capacity 3 ÷ 6 m^3/h(variable speed), power 2.9 kW.

- belt washing :
  installed n°1 centrifugal pump,capacity 160 l/min at 6 bars, power 2.2 kW.

alternative b/3 : sludge drying beds

- loading factor 150 kg DS/m^2 of bed per year (adopted)
- annual sludge production = 2,400 x 250 = 600,000 kg DS (see note)
- sludge drying beds surface = 600,000 : 150 = 4,000 m^2

Installed n°10 beds 10x40 m .

note : 250 working days/year adopted.

° ° ° ° ° ° ° ° ° ° ° ° °

ABBREVIATIONS

The following symbols and abbreviations are employed through this paper:

- **°C** : degree(s) Centigrade;
- **cm** : centimeter(s);
- **Eq** : Equivalent(s);
- **g** : gram(s);
- **h** : hour(s);
- **ha** : hectare(s);
- **hp** : horsepower(s);
- **l** : liter(s);
- **m** : meter(s);
- **min** : minute(s);
- **Mw** : molecular weight;
- **N** : Normal;
- **rpm** : revolutions per minute;
- **SC** : Standard Conditions;
- **sec** : second(s);
- **sp.gr.** : specific gravity;
- **V** : Volt(s);
- **W** : Watt(s).

Unit prefixes:

Symbol		Multiples and submultiples	
- **μ**	:	micro	(10^{-6});
- **m**	:	milli	(10^{-3});
- **k**	:	kilo	(10^{3}).

Other abbreviations:

- **BOD_5** : five days Biochemical Oxygen Demand;
- **COD** : Chemical Oxygen Demand;
- **DO** : Dissolved Oxygen;
- **DS** : Dry Substance;
- **SVI** : Sludge Volume Index;
- **TKN** : Total Kjeldahl Nitrogen.