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DRAFT PROJECT FINAL REPORT (IN 2 VOLUMES)

ENVIRONMENTAL CONSIDERATIONS IN THE LEATHER PRODUCING INDUSTRY 1/

VOLUME II

MEASURES TO MITIGATE THE ENVIRONMENTAL IMPACT OF THE LEATHER INDUSTRY

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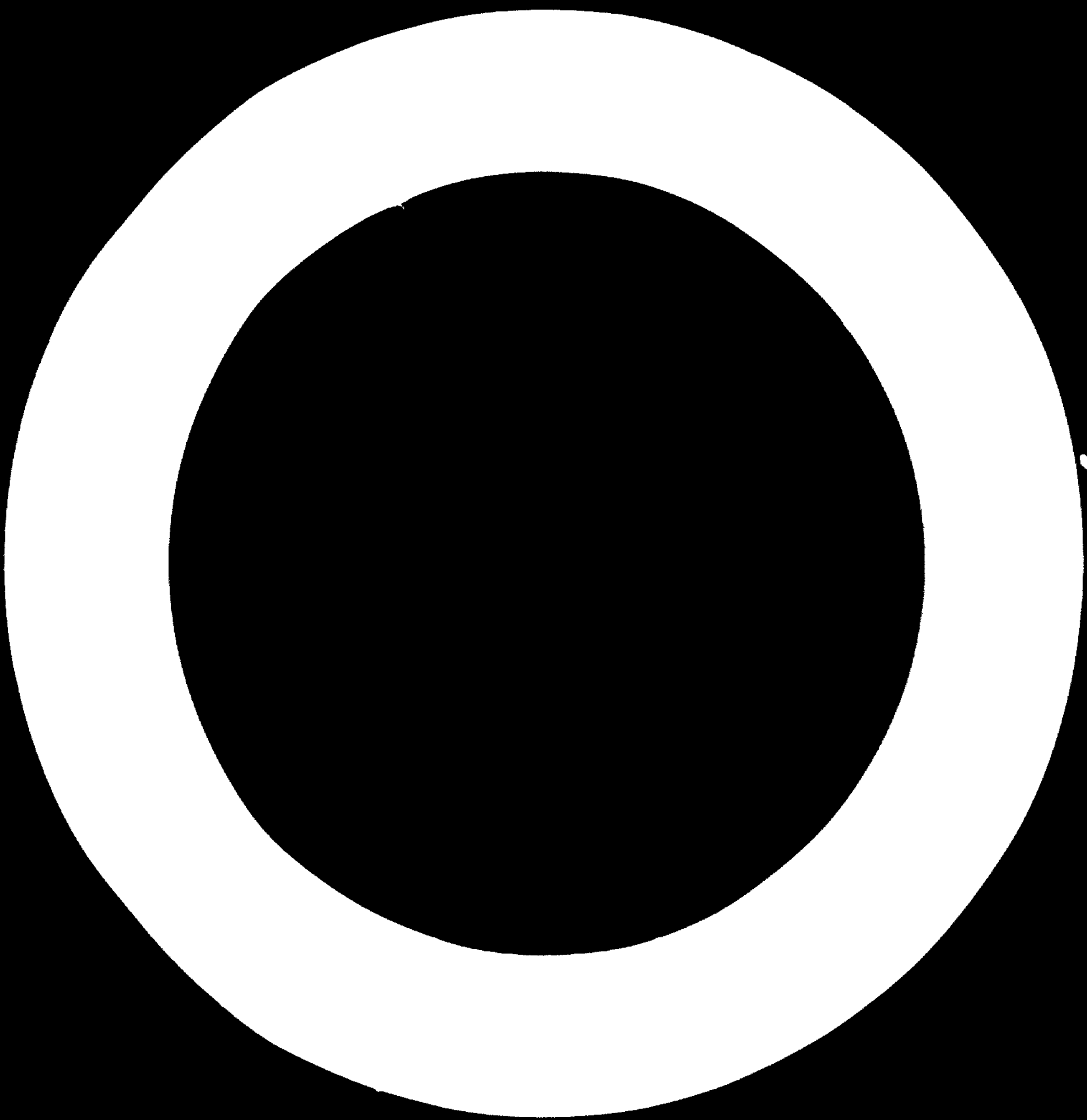

CONTENTS VOLUME II

INTRODUCTION

Following the United Nations Conference on the Human Environment held at Stockholm in 1972, the General Assembly of the United Nations established the United Nations Environment Programme (U.N.E.P.). The United Nations Industrial Development Organization (U.N.I.D.O.) with its special role in the field of industrial development has collaborated with the newly formed UNEP to form a joint work programme within the environment field. The project to which this report relates is a component of this joint study programme.

The major objective of this study within the leather sector, which from time immemorial has been universally recognised as having great pollution potential, is given in the project document as follows :-

"To study the leather industry in depth, in order to assess the environmental considerations which have an impact upon its operation and development. The study will be of a background and "stocktaking" nature which is necessary for formulation of an environmentally sound development in this branch of the industry."

Suggestions were sought at meetings from the representatives of several developing countries, in order to formulate a work plan to maximise the utility of the final report to the developing countries, especially where the leather industry is now, or potentially, is of significant economic or environmental impact.

D. Winters (United Kingdom) was appointed as Senior Consultant to co-ordinate the project and to edit the project report, and he was assisted in varying degrees by consultants, and the report owes much to the inputs of the following :-

Teferrra Assrat	(Ethiopia)
D.A. Bailey	(U.K.)
W. Frendrup	(Denmark)
T.J. Johnson	(U.K.)
T. Mathews	(India)
J.A. Villa	(Argentina)
W. Weber	(Switzerland)

Due to the large mass of material accumulated, and the wide span covered in the different chapters, and the divergent areas of interest it has been felt expedient to report on the project in two volumes.

Thus Volume I deals with the more generalised situation, including the possible environmental impact of the industry, treated theoretically, and based on three area studies, as well as the financial implications of the introduction of control plant and equipment.

Volume II has a more technical treatment and aims at mitigating the harmful environmental effects of the leather industry, giving some detail as to means by which environmental impact may be lessened by employing "best environmental processes", and also outlining possible effluent treatment systems applicable in differing circumstances.

Thus Volume I is addressed to governmental and industrial decision makers, and Volume II is of more concern to the entrepreneurs and technologists, as well as the planners. Both Volumes, however, are closely interrelated, and need to be read in conjunction with each other by those who wish to implement any specific proposal.

In general the report is directed towards the developing countries where the tanning industry in many cases is undergoing expansion. However, much of the data is pertinent to the more developed nations although in these areas more sophisticated and costly treatment schemes may be employed.

The recommendations outlined in Volume II are given as general guides - treatment plants have not been operated under the exact conditions quoted but international authorities in this field agree that in most instances the proposed treatment plants should operate efficiently, subject to some minor local modifications.

Volume II is composed of two major parts:

Part I - Chapters I-VI inclusive, dealing with the introduction and advantages of "better environmental" processes applicable to the manufacture of leather; and

Part II - Chapters VII-X which concerns itself with the treatment of effluent from two tannery models, which have been used in previous UNIDO publications:

An Upper Leather Tannery with daily input of 1,200 African Hides (ref: ID/WG.157/11), and

A Sole Leather Tannery with daily input of 200 Hides per day (ref: ID/WG.157/9).

Treatment schemes are suggested for these two tanneries at different locations, e.g. urban and rural. Introductions to these parts of the Volume are therefore made separately - see Chapters I and VII.

An introduction to the UNEP/UNIDO Project relating to the leather industry and its impact on the environment, and some summary of the conclusions may be found in Volume I of this report.

VOLUME II PART I

CHAPTER I

BEST ENVIRONMENTAL PROCESSES

ENVIRONMENTAL CONSIDERATIONS IN THE LEATHER INDUSTRY

BACKGROUND NOTES

It was found expedient to discuss here two major types of leather production, viz. the production of chrome upper leather, and of vegetable sole leather.

The effluents from the production of other chrome leathers, e.g. upholstery or clothing produce similar effluents to the upper leather production.

The effluents from the production of vegetable "semi tanned" or crust leather are substantially the same as the effluents from vegetable sole leather production. Such minor differences as are found will be treated separately.

For the sake of simplicity it is assumed that the split is tanned in the same way as the grain. In practice the split may be tanned in a different fashion from the grain leather, or may be sold for processing elsewhere, but in that case the necessary corrections may be made.

A special effluent problem arises from the degreasing of sheep skins or pelts. The effluents from the degreasing contain, in addition to the fatty substances from the skin, greater or smaller amounts of organic solvents and/or detergents, also neutral salts which render special measures necessary.

Methods of raw hide preservation influences the amounts of pollution from the tannery greatly. Three types of raw material have been considered: wet salted hides or skins; air dried hides or skins; and hides or skins which are processed fresh or short-time preserved with small amounts of disinfectants, e.g. sulphites, biguanides (Vantocil I B) or other chemicals. The last mentioned type is not commercially used at present, but may gain ground because of the effluent problems resulting from salt preservation.

The individual processes for the above mentioned types of leather manufacture are discussed below with regard to minimization of pollution. Possibilities of combining two processes or more are also discussed. Only technologies which have been sufficiently tested in practice, or can be assumed to be developed for industrial use within a few years are discussed. Ideas or suggestions which are supposed utopian or futuristic are omitted.

The question of what process is utopian or futuristic is not easily decided. In this context one may view the new vogue of technology incorporating recycling of the major polluting processes which many experts feel is on the verge of commercial acceptance.

These recycling processes which can have significant beneficial effects on pollutants discharged and costs of leather production are discussed under the general heading of "Best Environmental Processes". Although, as they are not yet fully accepted by industry, they have not formed a major part of the presentation and the discussions in this report have referred in general to the best environmental processes currently accepted for commercial leather production. However, there is little doubt that when the work in this field, in several institutes of the world, in due course, comes to fruition, the treatment of tannery effluents may be much simplified, with the resultant lessening of costs. Indeed one may quote from a recent meeting at the Centre Technique du Cuir (C.T.C.), reported in LEATHER*(i) referring to two major recycling processes, suggests that ..."The use of these two modifications, plus the use of counter-current washing was claimed to reduce total water consumption from 13.5 to 8.3 m^3/ton*(ii) in addition to bringing about a major reduction, perhaps as much as 80%, in the toxicity charge."

A further new technology being developed is the recycling of waters within the tannery following varying levels of treatment of the discarded liquors. Recent experiments in both pilot plant and tannery give hope that in the near future some relatively simple to operate, economic, process will allow recycling of treated waters within a tannery.

However, in the realisation that such new technologies are unlikely to be available in the mass of tanneries in the developing countries for many years, and even in newly installed tanneries such techniques may not be employed for five to ten years; hence it is felt more appropriate to consider offering advice aimed at improving the more conservative conventional processes currently accepted by tanners, in an effort to lessen their environmental impact.

Considerations of the individual processes are synthesized to a form of "environmentally best" practicable technology for the production of the types of leather mentioned above, and calculations of the amounts of pollution

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*(i) LEATHER (International Journal of the Industry, London, April 1975, No. 1774398 Page 59)

*(ii) m^3/ton is equal to l/kg

resulting from the use of these technologies are made. The figures are only "typical" or "average" as no two tanneries will adopt exactly the same technology or use the same type of raw material.

It is necessary to relate the amounts of pollution stated below to some well defined reference quantity. It would seem natural to use the green weight (the weight of the fresh slaughtered hide); but as most tanners calculate on the basis of the raw materials delivered to them, and most of the information accessible consequently refers to the salt weight (the weight of the salted, drained hide), this has been chosen as reference quantity in the present report. Figures related to dried hides or fresh or short-time preserved hides are converted to the corresponding salted weight.

The conversion ratios between the weight of the hides or skins at different stages of production depend to some extent on the type of raw material and technology utilized, and in the present report the following conversion ratios are used :-

	% of salted weight
Green weight	115
Salt weight	100
Pelt weight (fleshed, not split)	120
Shaved weight (chrome grain leather)	35
Wet weight of Chrome Split	13
Weight of dried Hides or Skins	40

CHAPTER II

TANNING AND THE ENVIRONMENT - GENERAL

In Annex I figures for the effluent volume and amounts of pollution from tanneries in the developed countries around 1970-73 are found (hair-dissolving unhairing of salted hides or skins). The figures are "typical" or "average" values, the actual figures for an individual tannery may be between 50% and 200% of the figures stated.

These figures suggest that a substantial reduction of the water consumption in the tanneries has already taken place; the average consumption of water in a chrome tannery has gone down during the last decade from circa 100 l/kg salt weight to circa 60 l/kg, but amounts of pollution discharged with the effluent have scarcely been reduced during the period.

It is important to reduce both the water consumption and the amounts of pollution. The water consumption is important because of the raw water costs and availability, and because the dimensions and consequently the investment costs of some segments of an effluent treatment plant depend on the volume of effluent to be treated. Reduction of pollution is important because in this way the concentrations of toxic substances (sulphides, chromium, alkalinity) in treatment plant or recipient, and also the amounts of sludge from the effluent treatment, are diminished.

A. Water consumption

In a "typical" chrome tannery as referred to above, only about 40% of the total volume of effluent, or only about 24 l/kg salt weight is due to the wet processes. The remaining 36 l/kg are used for rinsing and various miscellaneous purposes.

A liberal overuse of water has unfortunately always been characteristic of the leather industry. From time immemorial tanneries were located in places with abundant supplies of water, and formerly the "overuse" may have constituted some 80% of the water consumption. Rationalization of leather manufacture in recent times, so useful in other respects, has also its environmentally disadvantageous aspects through the tendency to flush all waste down the sewer.

Some "overuse" is a necessity; some water is consumed by paste or vacuum drying (although this water may be recycled to a considerable extent) and also by the finishing processes, and water has to be used for sanitary purposes and the necessary cleaning of machines and premises too, although these uses are somewhat minute when compared to actual volumes employed in tanneries.

But the characteristic vast overuse of water results under normal circumstances from bad "housekeeping", and can be greatly reduced by measures which in priniple are quite simple. Overflow of the process vessels and the constant running taps and hoses must be eliminated. Pipe outlets must be reduced to the size necessary (a two inch pipe provides 0·25-0·3 m^3/min.); the hosepipes may be equipped with spring valves. The floor may be swept instead of being continually flushed over (flushing the floor once a day must be accepted for hygienic reasons). Leaky or faulty equipment must be repaired or replaced without undue delay. The use of an automatic control system for the dosage of water and chemicals (as marketed by e.g. Hüni & Co., Switzerland (1)), limits the flow of water for processing, but such sophisticated aids are not essential. Good housekeeping requires employee participation and adequate training to acquaint operators with the importance of eliminating all sources of waste.

The use of batch washing (in drums) instead of continuous rinsing with lattice door has been systematically investigated by the Dutch T.N.O. Leather Institute (2) (3) which found that the replacement of continuous rinsing by batch washing saves a considerable amount of water (50% or more of the total), additionally saving time and rendering possible a distinctly improved uniformity of operation.

Folachier (4) (5) gives detailed figures for the water consumption in two similar tanneries (Annex II) of which one uses continuous rinsing the other batch washing. In the first tannery the total consumption is 100 l/kg salt weight, in the other 25 l/kg.

Also the process water consumption can be influenced very much by the choice of technology. Short or no float techniques should be preferred, although in some cases a too short float can be detrimental (6), especially in full grain aniline leather as if the float does not cover the leather any casual stoppage of the drum may cause serious staining.

Generally, drums or mixers (hide processors) should be preferred to pits or paddles which demand much longer floats (300% of the hide weight or considerably more). It may be necessary however to carry out some processes in pits, e.g. the first soak of dried hides. The paddle has its natural use in the processing of long haired skins to avoid entanglement of the hairs, but in order to save water its use in normal leather production should be avoided.

Discussion continues between tanners as to whether drums or mixers are preferable. Compared to the drum, the mixer renders saving of water (and consequently of chemicals) possible, and requires a somewhat less floor to ceiling height (but a somewhat greater floor space); but the investment costs for a mixer are nearly double the costs for a drum of the same capacity.

Below the individual processes are discussed assuming the use of drums. A separate section covers such savings of water and chemicals as may be obtained by the use of mixers or other unconventional equipment instead of drums.

In connection with the establishment of a new tannery it is reasonable to consider recycling and reuse of water. Possibilities for this are discussed in Chapter VB.

B. Amounts of pollution

It appears from the figures in Annex I that the normal processing of the salted raw hide to leather brings with it substantial amounts of pollution. This pollution arises from three fundamentally different sources :

1. Such constituents of the raw hide which must be removed during the leather processing, i.e. the hair substance, the non-collagenic proteins and fat from the hide, together with the salt which in most cases is used for preservation of the raw hide.
2. The (minor) amounts of pollution arising from sanitary purposes, from the cleaning of machines and premises and from any use of water as a medium of transport. Also solids dissolved in the raw water which stay in the effluent, are included here.
3. The chemicals used in the production.

The polluting constituents mentioned under 1 above arise necessarily from the leather production. The non-collagenous components of the raw hide must be removed to ensure the necessary good quality leather. A reduction of these amounts of pollution demands a radical reorganization of the leather production, i.e. suppression of the salt preservation and/or the introduction of a hair-saving unhairing.

The constituents mentioned under 2 may to some extent be diminished. The maintenance of sound sanitary and hygienic conditions brings with it an amount of polluted effluent. But the amount may, with good housekeeping, be kept to a reasonable minimum level.

The amounts of pollution mentioned under 3 should be reduced to the greatest possible extent. It has been normal practice for the tanners to pay for vast surplus amounts of chemicals which enter the sewer and pollute the recipient without being of any use in the factory; a practice arising from tradition among the tanners aided by good salesmanship from the chemical companies. Consideration for both the environment and the resource economy should force minimization of process chemicals. This may be done by minimizing the dosage of chemicals to the individual processes and/or combining several treatments into one single process.

The amounts of pollution (point 1 and 2 above), which are inevitable (theoretical minima) may be estimated as follows for a chrome tannery, in g/kg salt weight.

Inorganic (fixed) solids:	Hide salt	150 g/kg
	Salts from hide, raw water, sanitary use	10 g/kg
	Total	160 g/kg
Organic (volatile) solids:	Hair protein	40 g/kg
	Hide protein	25 g/kg
	Hide fat & carbohydrates	15 g/kg
	Dirt & manure	5 g/kg
	Organic substances from raw water & sanitary use	2 g/kg
	Minimum of cleaning of machines & premises	3 g/kg
		90 g/kg
	Total solids:	250 g/kg

If one compares these figures with the "typical tannery effluent" Annex I one will find the typical tannery effluent some twice the theoretical minima. However the waste of chemicals cannot be completely abolished so that the theoretical minima cannot be obtained in practice.

CHAPTER III

BEST ENVIRONMENTAL PROCESS - CHROME UPPER LEATHER PRODUCTION

A Raw Hide Preservation

In the developed countries raw hide preservation is normally not carried out in the tanneries, and the pollution from this process is not included in the figures in Annex I. But raw hide preservation is most often a necessary part of the conversion of the raw hide into leather and consequently it has to be considered in this context.

During salting about 40% salt is offered (NaCl, often with addition of 1 - 3% soda ash and naphthalene) calculated on the green weight, (corresponding to about 45% calculated on the salted hide weight). The salt distributes itself as follows:

	% of salted hide weight
Bound in the hide	15
Can be brushed or shaken off	22·5
Drains off at the preservation	7·5

The salt bound in the hide is found in the effluents from soaking and, to a smaller extent, unhairing in the tannery.

Often much of the salt which is brushed or shaken off arrives in the sewer. This is bad practice and must be prevented; at least in inland factories.

The volume of drain water from the salt preservation amounts to about 0·3 l/kg salted hide weight and carries with it the following amounts of pollution:- (7) (8)

	g/kg salted hide weight
Total solids	90
Hide salt	75
Protein	5 - 10
Fat	5 - 10
BOD_5	3·9
COD	7·4

Brine curing will result in almost the same amount of pollution being discharged as scatter salting.

In case of preservation by drying (or processing of fresh hides), the organic substances which would otherwise have been extracted by the salt, appear instead in the effluent from soaking and unhairing (7). If drying is carried out unsuitably, the amount of proteins extracted will rise at the expense of the yield of finished leather substance.

The question of neutral salts content in effluents has already been discussed in Chapter III Vol 1. Methods for desalination of effluents, e.g. reverse osmosis or destillation are at present uneconomic for use in tanneries, but may on a longer view come into practical use under especially disadvantageous conditions (dry climate and inland situation) and in that case the desalted water can be reused in the production.

With regard to the effluents, raw hide preservation by drying or immediate processing of fresh hides would be the best solution, but such drying involves a risk of deterioration of the hide substance, and consequently cannot be recommended for general use. Immediate processing of fresh hide will presumably be used in exceptional cases for practical reasons only (under tropical conditions this is risky).

The use of short-time preservation of the hide [9, 10, 11, 12, 13, 14, 15] may be expected to gain ground, but this method too may involve effluent problems, if the disinfectant used for the preservation has a toxic effect in biological treatment plants, or in the recipient. With regard to the effluent quality, milder agents, such as sulphites may be preferred to sodium pentachlorophate etc. used by Cooper [14, 15].

Fleshing and trimming at the slaughterhouse or some central hide curing plant before salting will reduce the consumption of salt and unhairing chemicals, and consequently the pollution load. The fleshing causes a loss of weight of 15 - 16% and a further loss of 1 - 4% results from a more than normally extensive trimming in connection with the fleshing, so that the weight of hides to be salted and unhaired is reduced by about 19%. Furthermore, the fleshing eases the penetration of salt and unhairing chemicals and in this way facilitates economic chemical usage

In addition, this practice has the advantage that the fleshings are not polluted with any chemicals, and consequently, are easier to process into meat meal compared with the normal, strongly alkaline, fleshings [16].

B Soaking

Soaking of salted hides may be carried out in drums. Van Vlimmeren describes a method for soaking salted, pre-fleshed (and cleaned) hides in one bath with 250% float [2]. It must be considered necessary to soak salted but not pre-fleshed hides in two stages: A wash for removal of dirt and manure followed by the real soak. The minimum length of each float may be 250% [17] or - more conservatively estimated - 300% [18] (calculated on the salt weight).

Soaking of salted hides normally does not require any addition of chemicals if it is carried out overnight. But if the soaking is to be completed within a few hours, enzymes and/or detergents have to be added to open the structure of the hide and facilitate water penetration. About 0·5-0·8% enzyme product can be used.

Dried hides are more difficult to soak; more time, more water and more chemicals are necessary. Dry hides should not be drummed during the first hours in soak because this would [illegible] them, and soaking in pits or [illegible] instead of drums may be accepted in some cases. For the first [illegible]0-1,000% float (on dry weight) is reasonable. Enzymes and/or detergents must be added (1-2% enzyme product or [illegible]% detergents may be used) [illegible] furthermore alkali (or perhaps acid) is added to expedite [illegible] and restrain the growth of bacteria. Also often a disinfectant [illegible] substance which acts both as a detergent and a disinfectant is added. Typically 1-2 g/l caustic soda - NaOH - or soda ash - Na_2CO_3. Soaking of dried hides with a common salt - NaCl - solution is used in some areas (19), but should be avoided by all inland tanneries.

The soak liquors contain a considerable part of the total pollution from the tannery derived from hide salt, blood, dirt and [illegible], plus fat and protein extracted from the hide. The pollution load from the soaking is greatly influenced by the preservation method and the condition of the raw hide, but hardly by the performance of the soaking itself. All that one can do in this respect is to minimize the use of water and of any auxiliary substances used.

A salted hide carries with it about 150 g salt per kg (17)(20). It has been stated that a salt content of minimum 140 g/kg salted hide is necessary for efficient preservation - of this amount about 25-30 g will be carried with the hide into the unhairing liquor. From the hide circa 5 g mineral substances and 15 g organic substances are extracted in the soak. The last mentioned figure may be much greater with extra dirty or extra fatty hides. The organic substances exert a BOD_5 of circa 12 g/kg and a COD of some 25 g/kg. The amount of (organic) nitrogen is about 1·5 g/kg (21), equivalent to circa 9 g protein per kg.

Unless pre-fleshed hides are used, the fleshing should be carried out after the soaking (green fleshing) and not - as is common practice at present - after the unhairing. Green fleshing has the same advantages as pre-fleshing with regard to pollution from unhairing and the quality of the fleshings. The improved penetration of the unhairing chemicals may result in a superior leather quality (22), (23). A major Scandinavian upper leather tannery has just introduced green fleshing for these reasons.

C. Unhairing

The unhairing process serves a twofold purpose; as is evident from the name, the hairs must be removed. Additionally the structure of the hide must be opened and non-collagenous proteins removed. Both actions are necessary for the production of good quality leather.

Of all tannery processes unhairing causes the greatest pollution load, made up of the dissolved hair substance, dissolved protein and fat from the hide, plus the unhairing chemicals (lime and sulphide) which are traditionally used in excess because such an unhairing system has the great advantage that use of excess chemicals does not lower leather quality.

A profusion of alternative unhairing agents has been proposed (enzymes, dimethylamine, chlorine dioxide, peroxides, sodium hydroxide etc.), but with regard to good leather quality and simple process planning no suggested method equals the hair dissolving lime-sulphide unhairing.

From an environmental viewpoint a hair-saving, no-sulphide method, should be preferred, but the use of such hair-saving methods involves problems e.g. a greater demand for time and manpower (the necessity of mechanical unhairing), greater chemical costs and, last but not least, difficulties with leather quality. In the production of good quality European type upper leather from cattle hides it has been said that it is not possible to use hair-saving unhairing (24) and notwithstanding its environmental drawbacks, the hair-dissolving method must be accepted, adequate effluent treatment being provided. For other purposes, however, including some types of skin processing, a hair-saving method can be used. Hence two technologies will be suggested, a "hair-dissolving" and a "hair-saving".

The use of lime and sulphide is the best method of hair-dissolving unhairing (25) (26) and necessary environmental improvements are obtained most suitably by a minimisation of the amounts of lime and sulphide used. Use of caustic soda - NaOH - instead of lime - $Ca(OH)_2$ - to diminish the amount of sludge makes it more difficult to control the unhairing, as an overdosage of caustic soda - NaOH - attacks the hide substance. Replacement of sulphide by other chemicals like dimethylamine (DMA) or mercaptanes (Mollescal SF, BASF) solves only the specific sulphide problems which may be solved more simply by oxidation of the sulphides in the used liquor. DMA dissolves the hair only in a strongly alkaline solution and consequently involves the same risk as the lime/sulphide method (27). Mercaptane unhairing (28) (29) has not been reported to work well in practice. A combination of Mollescal SF and [illegible] used in tannery practice, but presents no special advantage [illegible] the use of sulphides [illegible] Oxidative unhairing with chlorine dioxide [illegible] has not come into practical use in tanneries.

The amount of pollution from the hair-dissolving lime-sulphide [illegible]

[illegible]

[illegible] tannery practice [illegible] and many [illegible] to use vast surplus of lime and sulphide up to [illegible] lime and [illegible] 5 per [illegible] weight). This dosage can be greatly reduced without reducing the [illegible] effect or the leather quality. Much research has been [illegible] and the following dosages can be stated as generally sufficient for hair-dissolving unhairing in drums:-

Water [illegible]

Hydrated lime - [illegible]

[illegible] 5 % e.g. Sodium Sulphide - Na_2S [illegible])

[illegible] Sodium Sulphydrate - NaSH - [illegible]

In some cases the use of even smaller amounts of chemicals is possible. To some extent the minimum dosages of Hydrated lime - $Ca(OH)_2$, Sodium Sulphide - Na_2S, and Sodium Sulphydrate - NaSH are interdependent.

A reasonably long and careless drumming is necessary and it is advantageous to carry out the unhairing at a temperature of [illegible] (33, [illegible])

A reduction of the amount of chemicals used entails a substantial reduction of the amounts of pollution from the process. In Annex III amounts of pollutants from unhairing with two different levels of dosage are given (36).

"Hair-saving" unhairing can be carried out with small amounts of lime and sulphide with enzymes or with lime and dimethylamine. In any circumstances the opening of the hide structure through an alkaline swelling is a condition of obtaining good quality leather, and an enzyme unhairing (or any other non-alkaline unhairing) must be followed by or (37) combined with an alkaline treatment. It has been found to be of no importance for the amounts of pollution whether the two treatments are carried out separately or combined. (38, 39, 40)

[illegible]

[illegible] enzyme [illegible] [illegible]

[illegible] [illegible]. compared [illegible] the [illegible] figures [illegible] may seem [illegible]. The reason is that the enzyme treatment [illegible] more [illegible] the [illegible] of the hide than the lime sulphide treatment [illegible] even [illegible] a little [illegible] agent, but it must be understood that the enzyme treatment makes enzymatic bating unnecessary, and consequently must be considered more favourably than it appears from the table.

Even in effluents from "hair-saving" [illegible] sulphide unhairing small quantities [illegible] sulphide are found, arising from keratinous substances in epidermis and hair-roots. The figure in Annex III of [illegible] S kg salt weight refers to enzyme unhairing without any use of sulphide.

Any reduction of the amounts of pollution beyond the figures in Annex III for enzyme unhairing must be obtained through reuse of the unhairing liquor and/or precipitation of the dissolved protein plus perhaps unhairing in the soak.

A limited reuse of unhairing liquors has been long accepted because amines from the decomposed protein was supposed to have an unhairing effect. It has been said that because of accumulation of protein decomposition products reuse of the total liquor from a hair-dissolving unhairing is possible only about 10 times or less. However others report good results from 20 times reuse of the total liquor from a hair dissolving process in laboratory scale tests, (41) and Wiegand (42) describes a system which has been used in practice for four years. The total liquor from a hair saving paddle unhairing is reused. After each use it is replenished with 15% water, 0·5% Sodium Sulphydrate -NaSH - (ca 0·28% $S^{=}$) and 2·1% lime.

If the liquor from a "hair-dissolving" unhairing is sedimented the supernatant has been reused (30). A "hair-dissolving" drum unhairing with 100% water 1·5% Sodium Sulphydrate - NaSH - and 6% lime was used. After each use it was replenished with about 35% water 0·75% Sodium Sulphydrate - NaSH and 3% lime. The method has been tried in laboratory scale with good results, (33) (36) and is at present being tried on an industrial scale in Scandinavia. Estimated values for net use of water and chemicals and net amounts of pollution from this [illegible] are found in Annex III. The net reduction in the discharge of organic bound nitrogen is [illegible] g/kg salt weight. Of this some [illegible] g/kg is found in the finished leather (cf 44) which to some degree can modify the properties of the leather, and [illegible] g/kg is collected as protein product.

After each use replenishment with [illegible]% water, [illegible]% S and [illegible]% lime ([illegible]) is necessary.

Reuse of sulphide by driving off hydrogen sulphide - H_2S - from the used liquors and reabsorption in alkali as proposed by Blasej et al (45) cannot be recommended as the system was used for some years in a French tannery (46) but brought with it an accident with several deaths. Liberation of the extremely toxic and corrosive gaseous hydrogen sulphide indoors must be avoided.

The [illegible].N.O. Leather Institute advocates unhairing in the soak liquor. According to Herfeld and Schubert (47) the opening of the hide structure is insufficient when the unhairing is carried out by a common salt - NaCl - concentration greater than 2·5·0%; but this difficulty is obviated by giving the pelts a separate lime treatment. The pollution from the liming is small compared to the pollution from soaking and unhairing. The procedure may be as follows :-

Soaking + Unhairing :	150% Water + [illegible]% Fungicide
	Drum intermittently overnight;
	+ 3% Sodium Sulphide - Na_2S (60/62%)
	Drum four hours
Washing	10 min with 50% Water
Liming	250% Water
	4% Lime - $Ca(OH)_2$
	Drum intermittently
	Rest overnight

Thus 70-80% of the organic pollution from the tannery is collected in a volume of only 3·5 l/kg salt weight and is easily treated. The protein from the soaking-unhairing liquor can be precipitated by acidification and has good dewatering and filtering properties. The method is being attempted on an industrial scale.

Simoncini et al (48) (49) have tried to unhair the salted hides directly in the soak as follows :-

Soaking -unhairing :	Salted hides + 40% Water
	4% Sodium Sulphide - Na_2S (60-62%)
	0·8% Caustic Soda - NaOH

Soaking - unhairing continued:	0.3% surfactant
	Drum four hours
+	Water to 300%
	Drum two hours
Washing	300% Water

Fleshing, deliming etc.

For dried hides a pre-soak of six - eight hours and an addition of common salt - NaCl - to the soaking - unhairing liquor are given.

It is doubtful whether the soaking of the hides is perfected, and the available information regarding properties of the leather [36] are not too encouraging.

The total use of water and chemicals for soaking-unhairing-liming after the classical technology and these methods are:-

(% of the salt weight)

	Classical technology (as above)	P.N.O. *(1) Soak Unhair	Simoncini
Water	750	550	600
$S^=$	0.86	0.70	1
Lime	2	1	
Common Salt - NaCl	-	-	-
Caustic Soda - NaOH			0.8
Surfactant			0.3

None of these methods are fully developed industrially at present but a technology of this type may become realistic within the next few years. The only substantial advantage of this technology compared to the classical technology however is that it renders collection of the protein from both unhairing and soaking possible.

After unhairing two washings are given. The swelled pelts are vulnerable, and thorough cleaning of the grain is necessary.

Estimated average figures for the amount of pollution from the washing after unhairing (hair-dissolving lime-sulphide) are, per kg salt weight: 20 g total solids, 12 g fixed solids, 0.8 g total nitrogen, 0.5 g sulphide [48] [36] [44]. Frendrup found that in case of reuse of the unhairing liquor these figures were increased by : 10 g total solids, 3 g fixed solids, 0.6 g total nitrogen [36].

Generally speaking it is of no importance to the effluent whether the hide is split after liming or after tanning. Consequently this question is not discussed here.

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4. Deliming and bating

The deliming and bating liquor can be made up without or with a minimal addition of water, as water is carried with the pelts from the previous washing. Perhaps 5-30% water (calculated on the pelt weight) has to be added [14] [48] [50].

The minimizing of unhairing chemicals allows deliming chemicals to be kept at rather a low level, about 1 - 2%. Mixtures of ammonium salt and organic acids (e.g. sulphophthalic acid) or Sodium Bi-sulphite $NaHSO_3$ may be used. In some cases (eutrophication of the recipient) it may be necessary to minimize nitrogen in the effluent, and in such cases, the use of ammonium salts for the deliming should be avoided.

The bating agent is added amounting to 0·5-1%.

Washing after the deliming-bating is necessary to prevent mineral substances from unhairing and deliming being carried with the pelt into the pickling-tanning liquor. This is specially important when the tanning liquor is to be reused. The length of the float can be held at about 200% or less.

The effluent from deliming-bating contains residues of the chemicals added, sulphide and calcium from the pelt and protein (decomposed by the bating enzymes). The amount of sulphide is 0·1 g/kg salt weight, the amount of organic bound nitrogen extracted from the pelt about 0·6 g/kg salt weight [48].

If enzyme unhairing is used, the bating is superfluous, and the amount of nitrogen which otherwise is extracted in the bating, is, in this case, extracted in the enzyme unhairing.

New methods to replace deliming, bating and pickle have been proposed [51]. After fleshing and washing, the pelt is treated with 2·5-3% of a polyphosphate-citric acid- mixture in 80% water and 2-2·5% Formaldehyde - HCHO (30%) is added. After this deliming and pretannage the pelt can be pickled without salt prior to chrome or vegetable tanning.

5 Pickling and chrome tanning

The pollution from these processes consists of chrome (not fixed in the leather) and salts (from the pickle and from the chrome tanning product, and from acid and alkali added in pickle and basification). In addition to these pollutants there are minor amounts of protein extracted from the hide.

Pickling and chrome tanning should be based upon a system of short duration pickling and tanning in the pickle liquor. A short duration pickle gives better chrome uptake and better leather quality than an equilibrium pickle [illegible].

A reduction of the chrome discharge from a tannery can be obtained in three ways :

1. Improving the chrome fixation (not only the chrome uptake!)
2. Reuse of the chrome liquors (as appears from above, this should be done by making up a new pickle in the used tanning liquor.)
3. Precipitation of chrome from the used liquors with alkali, redissolving and reuse of the chrome precipitate.

An improved uptake and fixation of chrome can in principle be obtained through:

Decrease of the acidity of the pickle and increase of the basification after the tanning.

Decrease of the amount of neutral salts present during the chrome tanning.

Decrease of volume of tanning liquor.

Decrease of chrome dosage

Increase of temperature at the end of the tanning

Increase of tanning time

Presence of certain chemicals (e.g. oxozolidone) during the tanning.

In typical practice 2·5% Chromic Oxide - Cr_2O_3 calculated on the pelt weight (circa 20·5 g Cr/kg) salted weight is offered. Of this offering some 25% is discharged with the used tanning liquor and 10% with drainage and effluent from washing, neutralizing and retanning. Thus only some 65% is fixed in the leather (grain leather, split and shavings). As the discharges of chrome from the following processes are influenced by the performance of pickle and chrome tanning they too are treated in this section.

Consideration for the leather properties constrains the extent of variation of the conditions mentioned above. It is however possible to produce a good quality side leather with an offer of 2% Chromic Oxide Cr_2O_3 (on pelt weight) and to obtain a fixation of 84% of the chrome, when 13% is discharged with the tanning float and 3% with the effluent from the subsequent processes. In Annex IV chrome balances are given for "normal" chrome side leather production and for a technology of this kind.

A practical technology which entails this degree of fixation is the following (53) (54):-

Pickle 25% Water
3% Common Salt - NaCl
1·1% Formic Acid - HCOOH (85%)

Tanning: + 7·5% Commercial Chrome Tanning Salt

Basification: + 0·75% Sodium Carbonate - Na_2CO_3

1·1% Sodium Sulphite - Na_2SO_3

Self-basifying chrome tanning agents may be used instead.

The use of salt in the pickle can be entirely avoided by the use of non-swelling organic acid, e.g. b-naphthalenesulphonic acid (about 1·5% on the pelt weight) or with polyphosphoric acid.

Toward the end of the tanning the temperature is increased to approximately 70°C. The temperature should only be increased after the pelt has reacted sufficiently with the chrome because non-tanned pelt cannot stand high temperatures.

Schubert [55] states that it is possible to pickle without salt by using only 5-10% float. Later the chrome tanning agent is added dry to the pickle. The volume after the tanning is about 40% becuase the pelt liberates some water and some water is also added in the basifying. The chrome uptake is 65-80%.

Zissel et al [56] propose the use of salts from the deliming in the pickle and to dry pickle with a solid organic acid (oxalic acid) without addition of salt. The tanning agent is added dry and the tanning is completed with a float of 8-10%. By offering 2% chromic oxide (Cr_2O_3) on the pelt weight only 2% of the chrome remains in the float. However, 3% is discharged with drainage and 8% with the washing waters. If a loss of 1% is added to this due to neutralization and retanning, the total chrome fixation is some 86%.

In the future, the degree of fixation achievable may be increased to about 92%, but hardly further. At present however 85% fixation must be regarded as the practical achievable maximum. The discharge of chrome corresponding to this about 2·6 g Cr/kg salt weight cannot always be accepted.

The above discussion refers to side leather production; in boxcalf processing greater amounts both of tanning agent and of water are used, and consequently the exhaustion is less. In a Scandinavian boxcalf tannery 2·8% Chromic Oxide - Cr_2O_3 - on the pelt weight is used, of which only 58% is fixed in the leather, corresponding to a discharge of 9·7 g Cr/kg salt weight.

Use of the chrome liquor for making up the pickle has been investigated in several places [30,57,58,59,60,61] and is about to gain a foothold in the tanneries.

Through this method the amount of chrome which would otherwise have been discharged with the tanning liquor can be recovered. According to Annex IV this makes up 25% of the amount offered. In practice the saving is only 20-22%. The percentage saving of basifying agents is the same as the saving of chrome. A minor saving of pickle acid can also be obtained. According to Davis and Scroggie [58] the used tanning liquor can completely replace the salt added to the pickle, but experience elsewhere [57][61] suggests one has to replenish with a small amount of salt.

Using such chrome/pickle recycling techniques one may obtain the following:-

	Gross Dosage	Net Dosage
Common Salt	6·0%	0·6%
Sulphuric Acid	1·5%	1·3%
Chrome Tanning Salt	10·0%	7·8%
Soda Ash	1·0%	0·8%
Sodium Sulphite	1·5%	1·1%

The discharge of chrome with the effluent will be about 2·7 g/kg salt weight.

In the liquor, an accumulation of sulphate ions, entering with the pickle acid and from chrome tanning agent, will take place. The total content of anions is not altered (Common Salt - NaCl - in fact is added to keep it constant), but the balance between sulphate and chloride ions will shift in favour of the sulphate. If the sulphate concentration becomes too high the leather will be stiff due to calcium sulphate - $CaSO_4$ precipitation in the inner layers of the leather. This can be avoided by using little or no Sulphuric Acid - H_2SO_4 for the pickle or by precipitating the sulphate from the liquor with calcium formate before reuse [57]. The Calcium Sulphate - $CaSO_4$ precipitated can be removed by a simple decantation or straining.

When using a "normal" chrome tanning process the savings of chemicals alone may cover recycling costs. This is not so using high chrome fixation methods, but reuse can also be practised in that process. Thus it should be possible to reduce the discharge of chrome to some 0·9 g/kg salt weight. A method of this type has been proposed.

An alternate to direct reuse of the liquors for the cautious tanner may be to precipitate the chrome from the used liquors with alkali, filter off the precipitate and dissolve it in acid for reuse [61, 62, 63, 64, 65, 66]. Compared to direct reuse this method has the advantage that the chrome is refined before reuse so that no accumlation of interfering substances occurs. This has been proven for many years in practice.

The disadvantages of the method are that no savings of pickle salt or acid are obtained and additional salts from the precipitation and redissolving are discharged. Further the filtering equipment is expensive and such a method is consequently suited only for large tanneries with a high content of chrome in the used liquors, e.g. boxcalf tanneries.

Minor amounts of chrome remain in the supernatant from the chrome precipitation, a discharge of circa 0·05 g/kg salt weight is to be reckoned with. This is only of minor importance compared to the discharge from washing and retanning (circa 1 g/kg salt weight).

F **Post Chrome Wet Processes**

These consist of four processes: neutralization, retanning, fatliquoring and dyeing plus the necessary washings.

Environmentally, it would be best to combine all four treatments into one short float process as described by Folachier [67] and Zissel et al [56]. But, as pointed out by, among others, Herfeld and Schmidt [68] salts from neutralization and retanning may interfere with the processes of fatliquoring and dyeing. Combining into two operations, neutralization-retanning and fatliquoring-dyeing, with an intermediate washing to remove the salts is in any case to be considered feasible, and has the advantage that it is possible to collect the chrome containing effluents from neutralization-retanning for separate treatment if necessary.

It is primarily through the post tanning treatment that the leather is given the character required and consequently no standard technology can be drawn up. The dosage of tan, fatty substances and dye varies within wide limits, and vegetable, synthetic, mineral or aldehyde tanning is used. The following can be regarded only as an "average" technology :-

	Percentages on shaved weight
Washing:	300% Water
Neutralization-Retanning	50% Water
	1% Sodium Bicarbonate
	5% Tan (Veg/Synthetic)
Washing	200% Water
Fatliquoring-Dyeing	100% Water
	5% Fat
	0·5% Formic Acid - HCOOH
	1% Dye
Washing:	200% Water

For the processing of split somewhat greater amounts of water and chemicals are used.

If one calculates 0·35 kg shaved grain leather and 0·13 kg wet split per kg salt weight, the total discharge from the after treatment will be about 4·3 l water, 5·5 g fixed solids and 24·1 g volatile solids (or totally 30 g solids) per kg salt weight (0·4 g chrome compounds from the leather included).

For a tannery which processes the grain leather only, the discharge will be 3·0 l water, 3·2 g fixed solids and 16 g volatile solids per kg salt weight.

G Drying and finishing, Sanitary and Others

Vacuum drying, pasting, finishing, sanitary purposes and cleaning of machines and premises all involve some water consumption.

In the vacuum drier water is used for the vacuum pump and for the condenser. The water for the vacuum pump mixes with the condensate from the leather and has to be discharged, whereas the water for the condenser is used for cooling only and can be recycled.

In a U.S. tannery about 7 l water per kg salt weight was used for vacuum drying [69]. Other investigations suggest the use of water can be circa 0·75 l/kg salt weight for the vacuum pump and circa 3·25 l/kg for the condenser [70].

The gross use of water for pasting (for washing plates and leather) is circa 3 l/kg salt weight. The water can, however, be recycled for a week so that the net discharge is circa 0·6 l/kg salt weight. The paste used is discharged with the effluent. The amount can be 2·7 g/kg salt weight of polysaccharides, exerting a BOD_5 of circa 1·4 g kg salt weight.

In some tanneries the buffing dust is flushed into the sewer. This practice is to be avoided as it is possible to collect the dust without use of water.

Some water is used in the finishing department. A reasonable consumption is 0·25 l/kg salt weight.

The consumption in the factory of water for sanitary purposes is (in developed countries) 125 l/man/day. Villa [70] gives the following ratio for leather production from hides: 17 sq. ft/man hour and 1·75 sq. ft./kg salt weight Supposing 7 hours work a day this suggests a water usage of :

$$\frac{125 \times 1{\cdot}75}{7 \times 17} = 1{\cdot}84 \text{ l/kg salt weight}$$

or approximately 2 l/kg salt weight.

For cleaning of machines and premises a consumption of 0·5 l/kg salt weight must be allowed.

Thus post wet work water consumption is estimated :-

	l/kg salt weight
Vacuum drying and/or pasting	1·0
Finishing	0·3
Sanitary	2·0
Cleaning	0·5
Total	3·8

When estimating the amounts of pollution discharged from the tannery one cannot leave out the substances contained in the raw water. The quality of raw water varies within very wide limits dependent on the character of the soil and the pollution of the water used.

The amounts found in practice are :-

	"Average" analysis of raw water mg/l	Assume floats of 20 l/kg salt weight g/kg salt weight raw material
Fixed solids	375	7·5
Volatile solids	75	1·5
BOD_5	10	0·2
Chloride	50	1·0
Sulphate	60	1·2

H Equipment for Wet Processing other than drums

Hide processors (e.g. the American concrete mixer or the French oblique homogenizing drum) may be used in practice for all wet processes in the tannery.

The hide processor has several environmental advantages over the traditional drum: It is possible to work with shorter floats and consequently to obtain saving of chemicals. Further, processors are particularly suited for the recycling of liquors, as they allow almost complete recovery of liquors from processed stock.

The survey in Annex V of the water consumption is compiled on the basis of published information on the water consumption by using hide processors [35, 58, 71, 72, 73, 74], and of practical use in some tanneries. For comparison the corresponding figures for a standard drum process are given. Additionally, figures are given for the equipment developed by Keller and Heidemann [1] [75].

It may be seen from the Annex that it is possible to save over [illegible] of the water by using hide processors instead of drums, (consumption for the total wet processing 20 l/kg salt weight with drums and [illegible] l/kg with processors). With the Keller-Heidemann apparatus the saving is less, among other things because this apparatus has a dead volume which must be filled in every process.

The use of hide processors also yields savings of chemicals, first and foremost of chemicals which must be present in a certain concentration in the float. Generally, savings of 10-20% of the chemical consumption can be obtained [[illegible]].

I Wet Blue and Crust Leather Production

The amounts of pollution from the manufacture of wet blue are the same as for the corresponding processes to chrome tanning inclusive as discussed earlier. To this some proportion of effluents from cleaning and sanitary purposes must be added.

The amounts of pollution from crust leather manufacture are the same as for complete leather production, with the exception of the discharge from the finishing, and up to half the discharge from cleaning and sanitary purposes.

CHAPTER IV

BEST ENVIRONMENTAL PROCESSES - VEGETABLE LEATHER PRODUCTION.

A Preservation, soaking and Unhairing

These processes are carried out in the same way as for chrome leather production. For the production of firmer leather the use of a lesser quantity of sulphide for the unhairing suffices (0·6-0·7% on the salt weight compared with 0·8-0·9% for chrome leather or more flexible vegetable leather). In many cases it is possible to unhair "hair-saving" with small amounts of sulphide (0·2-0·3% on the salt weight) (77) or with enzymes (19) (78) (79).

B Deliming

Deliming is carried out in the same way as in the chrome leather production. The pelt must be more thoroughly delimed for flexible than for more firm leather.

Normally the pelt is not bated. In some cases, however, in the production of flexible leather qualities, bating is carried out.

C Conditioning and Vegetable Tanning

Before the actual vegetable tanning the delimed pelt will undergo a conditioning which may be a pickling or a pretanning or both. For the conditioning a smaller quantity of acid will suffice than for the pickling before chrome tanning (e.g. 1% acid on the pelt weight). The treatment may be carried out in a drum (with about 150% float) or in a pit with standing liquor, which is strengthened after each use. The pretanning serves to improve the diffusion and fixation of the vegetable tanning agents. Chrome (0·25-0·5 Chromic Oxide - Cr_2O_3 on the pelt weight), formaldehyde (0·5-1%) polyphosphate (2-2·5%) or syntans can be used (80).

The available methods of vegetable tannage currently in use are numerous and one may only refer here to the two major styles: drum tannage and pit tannage.

The use of drums for vegetable tannage has in recent years gained popularity, and it may well be that this method of tannage is environmentally very sound. The use of drum tannage allows the use of smaller floats and is said to give a higher fixation of the vegetable tannage, thus one has lesser amounts of vegetable tannins in the effluent, or will have the tannins diluted with a smaller quantity of water and thus amenable to separate treatment.

Some environmentalists have questioned the wisdom of using chromium as a conditioner/pre-tan for vegetable tannage, but when offered at the low level suggested in the T.E.P.F. recently published process, i.e. 1% chrome tanning salt (0·26% Cr_2O_3 offer) at such chrome offer levels it is reported that the chromium fixation is high, thus only minute amounts enter the effluent. An alternative viewpoint suggests that even if only 30% fixation was achieved, the chrome thus discharged to the effluent from such a small offer would not pose any environmental problems. Following the conditioner pre tan drum vegetable tannage may proceed, using high tannin concentrations in the float thus yielding a rapid tannage.

From the traditional pit vegetable tanning in a counter-current pit system, a high proportion of the tannin is wasted with the effluent. The amount of pure tan offer was typically 35-40% on the pelt weight for sole leather and 25-30% for technical, case or upholstery leather. For the vegetable tanning of sheep or goat skins, only 12-20% on the pelt weight is offered. Of the tan offered, 20-35% is discharged with the effluent (81) (82). Moreover, most of the non-tannin compounds of the tanning extract are discharged too.

The utilisation of tannin can be ameliorated so that an offer of 30-33% tan may be sufficient for sole leather tanning. Drum tannage for lighter leathers offering 20% tan on the pelt weight (53) (80) have been developed.

Typical figures for the discharge from some types of vegetable tanning can be calculated as shown in Annex VI.

The amount of liquor discharged from a counter-current pit system may be about 100-150% on the pelt weight.

Various methods are used to speed up the vegetable tanning. A shortening of the tanning time will ameliorate the tannin utilisation because loss of tannin by standing is avoided. The fixation of vegetable tannins is increased by the use of some amount of syntan.

The RFP and C-RFP methods developed by Bayer AG (83) (84) involve pretreatment with a syntan (in the RFP method a syntan containing chrome, in the C-RFP method a syntan without chrome), succeeded by a vegetable tanning in drum without float. After the tanning 15 - 20% of a very concentrated liquor is left, carrying with it about 2·5% pure tan (on the pelt weight) out of an amount of 30·3% offered. With regard to effluents nothing can be obtained with this method beyond what is possible with the counter-current method except that the tannin is held in a greatly lessened volume.

Shuttleworth has developed a method for so-called no-effluent sole leather tannage (Liritan) (81) (82) (83). The delimed and washed pelt is pickled and pretanned in a standing liquor which is strengthened for each use with 1 [illegible]% Sulphuric Acid - [illegible] and [illegible]% polyphosphate. Subsequently, it is tanned in a closed system consisting of [illegible] pits at [illegible] days. For sole leather production about 35% pure tan is offered calculated on the pelt weight. After the tanning the leather is washed in a drum. It is asserted that the washing water can be used in a colouring pit or in the tan dissolving (84).

Atkinson (85) has developed an ultra-rapid procedure for vegetable leather tanning. The delimed and washed pelt is pickled with 5% Common Salt - NaCl, [illegible]-1% Sulphuric Acid - H_2SO_4 and [illegible]-1% Formic Acid - HCOOH [illegible]% in 15% water. Then the pelt is conditioned by drumming with 10% Sodium Sulphate - Na_2SO_4 without float and subsequently tanned with the addition of 50% water. After the tanning the leather is washed thrice with [illegible]-100% water.

The Liritan and Atkinson methods have been put into practical use and both methods are said to involve a very low effluent discharge from the tanning. Unfortunately, figures for the amounts discharged have been published for neither method. The Atkinson method is the most rapid and rational (the time for pickling, conditioning and tanning, all inclusive, is 3[illegible] hours). On the other hand, it involves the discharge of great amounts of Sodium Sulphate - Na_2SO_4 (10% onthe pelt weight or 12% on the salt weight) plus Common Salt, NaCl. This is no problem for tanneries situated at the sea, but for inland tanneries in a dry climate it may preclude the adaptation of the Atkinson method, although the Sodium Sulphate and the lime to some extent precipitate each other as Calcium Sulphate - $CaSO_4$. *(1)

D After treatment, Sanitary and others

After tanning the leather is washed in a short float and then bleached if necessary. Bleaching can be performed by drumming the sammied leather dry with a bleaching syntan (1-4% on the pelt weight) or a heavily bisulphited vegetable extract. Alternatively the leather is bleached by being dipped successively in a 0·5-1% Soda Ash - Na_2CO_3 solution, in water in a 0·5-1% Sulphuric Acid - H_2SO_4 (or oxalic acid) solution and again in water. The soda and acid baths can be replenished with chemicals after each use, but the washing water has to be changed regularly.

*(1) Sulphate may attack concrete and in stagnant areas may be biologically reduced to Sulphide. Thus limits of concentration of Sulphate in an effluent entering a sewer or a concrete structure should not exceed 1000 mg/l.

[illegible] estimated [illegible]

[illegible]

[illegible] Equipment [illegible]

[illegible]

CHAPTER V

BEST ENVIRONMENTAL PROCESSES - MISCELLANEOUS

A Degreasing of sheep pelt

There is a great divergence between the fat content of sheep from different countries. The wooled sheep prevalent in Europe, Australia, New Zealand and North and South America may well have a high grease content in their skins (in some areas over 30%). Hair sheep, traditionally from the Middle East and Africa, contain much lower quantities of fat within their skins.

The following notes refer in general to wooled sheep.

The fat is enclosed in fat cells which must be broken before the degreasing and consequently it is appropriate to degrease the pelt after dewooling and pickling (89). The most thorough degreasing is obtained by the use of organic solvent and emulsifyer, if necessary combined with a squeezing of the pelt whereas degreasing with a detergent or by pressing alone hardly suffice (89).

Typically, the following treatment is used:

Degreasing:	20% solvent (e.g. paraffin or white spirit)	
	1·5% monochlorobenzene	
	0·3% emulsifyer	
Washing:		
Twice with	200% Water	
	20% Common Salt - NaCl	

(percentage on the pickled weight).

The polluting substances are the solvent, the grease extracted and the salt. Organic solvents are very toxic in recipients and solvent and grease exert a very high oxygen demand (the COD of solvent and emulsifyer alone is circa 40 g/kg pickled weight).

25-30% of the solvent used can be collected as a clear liquor and reused (89) so that the net use of solvent will be circa 15% on the pickled weight. Circa 50% of the amount used is retained in the pelt after the first washing, and presumably part of this will be washed out and discharged from the subsequent processes. By pressing or centrifuging the degreased pelt half of this can be collected.

The amount of solvent collected, exceeding the 25-30% mentioned above, is found as a paste emulsified with the grease. The possibilities of absorbing this paste in buffing dust and burning this are being investigated.

[illegible] Water Reclamation System

Reuse of water can be [illegible] in two different ways: the effluent from some wet [illegible] operations can be collected and used for some other wet [illegible] operations without any intermediate treatment, or the effluent from all, or almost all, the processes can be collected and used as raw water in the factory after physical, chemical [illegible] biological purification [illegible] (89) (91).

In both cases it is convenient to keep the liquors from unhairing and from chrome or vegetable tanning separate and establish recycling systems for these liquors as described above.

The effluent from the second soaking has been used for the first soak, the water from washing after unhairing for the unhairing, and the water from washing after the neutralization for the washing before neutralization. In this way the water consumption was reduced from 37 to [illegible] l/kg salt weight, without any deterioration of the leather quality. Bailey has outlined a system with two storage and collection tanks, one for lightly polluted, and one for more heavily polluted effluent (90) (91). Pure water is used for unhairing, deliming, pickling-tanning and the after treatment only.

Systems of this type may be too complicated to be easily fitted into existing tanneries. Thus the effluents from the second washing after unhairing, the washing after the deliming and the washing from the after treatments could be collected in a storage tank and used for soaking, unhairing and the first washing after unhairing.

For the floats mentioned above the water balance will be as follows:-

Collected	% on salt weight
Second wash after unhairing	300
Wash after deliming	240
Washings from the after treatments * circa	350
Total	900

*Grain leather and Split

Used:

Soaking	500
Unhairing	200
First wash after unhairing	300
Total	1,000

In this way it is possible to save 900% on the salt weight. If the unhairing liquor is reused separately, the total saving is 800 + 150 = 950%.

By the use of mixers the balance [illegible]:

Collected:	% on salt weight
Second wash after unhairing	[illegible]
Wash after deliming	120
Washing from the after treatments *	200
Total	[illegible]

* Grain leather and split

Used:	% on salt weight
Soaking	150
Unhairing	100
First wash after unhairing	50
Total	300

The saving is 300% on the salt weight.

(This is in addition to the savings obtained generally by mixers as shown in Annex V)

The other method mentioned, collection, treatment and reuse of all effluents (except perhaps the effluents from unhairing and tanning) has been investigated in Italy (4-) (92) and Poland (93). Theoretically, this method is very attractive because it renders possible tanneries with totally, or almost totally closed water circulation. The method necessitates an expensive desalination after each use of the water (94) and chiefly for this reason it has not yet reached practical use, but it may come into use when the demands for effluent quality become so great that they exceed the demands for the quality of raw water for the tannery, e.g. if desalination is demanded.

As may be seen there is much scope for recycling of process waters both with and without treatment. The particular recyclic process adopted depends on tannery layout, whether pre-existing or being constructed, and processes employed.

In Annex IIII a diagrammatic outline of a direct recycling process is shown - a modification of Bailey's scheme mentioned earlier. It is suggested that tanners modify such processes to suit their own circumstances.

CHAPTER VI

BEST ENVIRONMENTAL PROCESSES - DISCUSSION AND CONCLUSION

On the basis of the earlier discussion the following frame technology for the production of chrome upper leather can be compiled (based on the use of drums). A technology of this kind should be commercially acceptable. In some tanneries it may be possible to save higher percentages of water and chemicals for some processes; in other tanneries it may be necessary to use somewhat greater quantities.

	Percentage on the salt weight
Soaking	2 x 250% Water
Fleshing	(Unless pre-fleshed hides are used)
Unhairing	200% Water
	2% Lime
	0·[illegible]-0·[illegible]% $S^{=}$
	(e.g. 2·5% Sodium Sulphide ([illegible]%) +
	0·5% Sodium Sulphydrate (90%))
Washing	2 x 300% Water
(Splitting)	Percentages on the pelt weight
Deliming-bating	15% Water
	0·75% Ammonium Sulphate - $(NH_4)SO_4$
	0·5% Sodium Bisulphite - $NaHSO_3$
	0·5-1% bating agent
Washing	200% Water
Pickling-chrome tanning:	25% Water
	3% Common Salt - NaCl
	1·1% Formic Acid (85%) - HCOOH
	+ 7·5% Tanning Agent (1·95% Chromic Oxide) - Cr_2O_3)
	+ 0·75% Soda Ash - Na_2CO_3
	1·1% Sodium Sulphite - Na_2SO_3
Sammying (Splitting)	15% Water
Shaving	
Percentages on the shaved weight	
Washing	300% Water
Neutralisation-retanning:	50% Water
	1% Sodium Formate Or Sodium Bicarbonate
	5% Tan (Vegetable or Synthetic)
Washing	200% Water

Fatliquoring-dyeing: 100% Water

5% Fat

0.5% Formic Acid (85%) - HCOOH

1% dye

Approximate amounts of pollution resulting from a technology of this type are quoted in Annex VII. Corresponding figures for vegetable tanning are given in Annex VIII. The Table refers to a counter-current sole leather tannage with good fixation. Presumably, considerably smaller amounts will be discharged by the use of the Liritan or Atkinson processes, but figures for this are not available. Also, considerably smaller amounts are discharged from the production of lighter vegetable leathers than from sole leather production.

The amounts of solids deriving from the raw water are quoted on the basis of the water consumption minus water used for unhairing, for washing after unhairing and for sanitary purposes. This is because the amounts of pollution for these fractions have been calculated from factual concentrations in the liquor, whereas the amounts for the other fractions have been calculated on the use of chemicals and the hide or hair constituents dissolved by the operation.

From the chrome leather production with the technology discussed here, circa 85 g suspended solids and 0·4 equivalent of alkalinity per kg salt weight are discharged against 150 g and 0·7 equivalent per kg in normal practice. By reuse of the unhairing liquor it is possible to eliminate the alkalinity almost totally.

The figures in Annex VII and VIII reflect mainly savings of chemicals; the amount of organic substance from hide and hair which must be discharged is the same as in normal practice. If necessary the organic pollution load can be diminished to some extent through replacement of formic acid and formates by other chemicals. In the same way, the discharge of ammonium salts from the deliming can be abolished by using other deliming agents.

Further reduction of the discharge can be obtained by changed methods of handling the raw hide, introduction of reuse systems in the tannery, and the use of hide processors instead of drums. What can be achieved through these means is shown in Annex IX - XII.

The use of green (or short time preserved) prefleshed hides is not likely to become general practice. It is treated here because it nearly eliminates the salt, and on the whole it is the environmentally most sound way of handling the raw hides. The figures in Annex XII (at least the figures for chrome leather production) represent the optimum of what is technically realisable today, but they will not be reached in many tanneries.

It is seen from Annex X and XI that a smaller saving of water is foreseen through reuse of both the unhairing liquors and the lighter polluted liquors, than through reuse of the lighter polluted liquors only. The reason for this is that it is found necessary when reusing the unhairing liquor, to use fresh water for both washings after unhairing. The reduction in the organic pollution load achieved by the reuse of the unhairing liquor has greater importance, however, than the slightly higher water consumption.

Annex VII - XII refer to typical processing of cattle hides into side leather or sole leather. As mentioned above great variations are found, and the figures can only be used with reservations for other types of leather.

The use of biocides and detergent in the tannery has not been discussed above. In Danish tanneries circa 0·35% biocide is used, calculated on the salt weight (variation 0·15-0·5%) (mainly of chlorophenols), chiefly in the chrome or vegetable tanning. Of the amount used half or more is bound in the leather. Often biocides are also brought into the tannery with the raw material. It is difficult to estimate what quantities of biocides from this source enter the effluent.

The total consumption of detergents in the tannery is about 0·1-0·5% on the salt weight.

VOLUME II PART II

CHAPTER VII

THE TREATMENT AND DISPOSAL OF TANNERY EFFLUENT

A. INTRODUCTION

This section of the report (Part II) aims to provide outline design data for purifying tannery effluents. The two models selected have been used as capital cost data is available for them in papers presented at UNIDO Seminars on Leather Industry development. These models relate to a vegetable sole leather tannery processing 200 hides/day (ID/WG 157/9), and a tannery processing 1,200 hides/day into chrome side shoe upper leather (ID/WG 157/11).

For each scheme four distinct stages of treatment are discerned, providing effluent of significantly improved quality at the end of each stage. In each of the two types of production considered, basically different treatment technologies are recommended as being appropriate for use in sparsely populated (rural) areas, and densely populated (urban) areas where space is likely to be considerably more restricted.

Where a choice is available the selection of non-sophisticated treatment methods has been made, as this report is aimed towards developing countries who are more likely to have available a pool of relatively cheap labour for excavations etc. It is pointed out that the existence of a pool of cheap labour does not eliminate the need for more sophisticated plant design where space is very limited: however, an effort has been made, when selecting treatment processes, to incorporate those which require the minimum of technical supervision.

It has been assumed that the pollutants in the effluent to be treated would be as in Annex I, with the major exception of quantity of water, this in Annex I is quoted as circa 65 l/kg, whereas for treatment it has been assumed that the usage is 15 l/kg (justified elsewhere), with a concommitant increase in concentration of the pollutants (see Chap. VIII and IX).

The plant designs are based on existing knowledge relating to the treatment of tannery effluent from conventional processing, but with appropriate allowances being made for the greater concentrations in pollutants resulting from the lower water usage. However, it is particularly stressed that there is no practical experience so far dealing with the accepted concentration of the tannery wastes, and the predicted performance of the treatment processes contains an element of speculation.

In Chapter V of Volume I may be found some costings, calculated in India, for the outlined schemes which may be of interest in other developing countries.

B Scope in Relating to Application of Data

All schemes are intended primarily as guidelines for costing and assessing spatial requirements where new tanneries are proposed or in cases where effluent treatment of existing factories is envisaged. In instances where individual treatments plants are to be constructed it will still be advisable to seek expert advice with regard to ground conditions, plant layout and the effluent quality standards which need to be achieved. Where it is intended to vary the production process for those cited in A above any possible change in treatability will also need to be taken into account.

C Technology Involved

The particular technology used in treating effluents will depend largely on the location of a particular factory. In rural areas where presumably more space will be available a literally "hole in the ground" approach has been adopted in the study; the shape and size of the holes depending inter-alia on the function required, e.g. sedimentation and anaerobic or aerobic treatment. Where appropriate (in the technical or financial sense) the basically "rustic" technique has been modified to incorporate twentieth-century technology. Thus, the use of simple mechanical aerators to increase the effectiveness of aerobic systems is suggested.

On the other hand, where less space is available, in urban areas, it is necessary to employ more sophisticated equipment. Nevertheless, even under such conditions an attempt has been made to keep equipment as simple as possible, in design and in operation.

However, it has been assumed that available land is not totally unlimited, and so methods of treatment which are particularly extravagant in land use have not been recommended. Treatment by land irrigation (except as a tertiary stage of treatment) would be a case in point; and in any event such a system would be environmentally very undesirable, especially in warmer climates.

D Primary Sedimentation

It is considered that primary sedimentation (settlement) for a minimum period of six hours in continuous flow dedimentation tanks, and for a longer period in lagoons, is the minimum treatment which should be received by any effluent prior to discharge; even when this is to a foul sewer. If the charges levied on the conveyance of the effluent and its subsequent treatment at a sewage works bear any relation to actual costs, it is almost certain that such primary treatment would also prove to be economically advantageous.

Primary sedimentation is of course highly desirable where subsequent biological treatment of the wastes is proposed in order to reduce the size of the biological stage. Even where this is in the form of an anaerobic or an aerobic lagoon, pre-settlement is essential to reduce the amount of biologically inert solids so that :-

1. the need for frequent desludging of the biologically active lagoons is avoided
2. the bacterial "wash out rate" is kept low, resulting in a more highly active lagoon.

Where biological filtration is proposed, pre-settlement of the wastes becomes essential to avoid clogging of the filter medium.

E Schemes for Use in Urban Areas

1. Primary Treatment

Very substantial reductions in the BOD and suspended solids content of tannery wastes can be effected by permitting the liquors to settle for several hours. Where space is restricted, sedimentation is most conveniently effected in specially designed tanks, which may be constructed using a variety of materials (reinforced concrete, brickwork, mild steel or even timber). The tanks may be of the horizontal-or-vertical-flow type (see Annex XIV Figs. 1a and 1b). Although more difficult to construct, vertical flow tanks have the advantage of being "self-desludging" when provided with sides sloping at an angle of 60 degrees; sludge being removed via a valve fitted at the base of the tank. Horizontal flow tanks, unless fitted with expensive sludge scraping mechanisms must be taken out of service, and the supernatant water decanted off, before the settled sludge can be removed. Manual removal necessitates the provision of one tank in excess of the number needed in service at a given time. Floating arm decanters are commercially available for use in this operation; however, a length of flexible hose supported a few cm. below the surface by an oil drum or a block of expanded polystyrene can be just as effective.

If funds are available for the purchase of mechanised sludge scrapers the use of radial flow sedimentation tanks, now widely used in developed countries, can be recommended as being economic both in space and labour.

It is important to be aware that the flow characteristics of sedimentation tanks are of paramount importance in determining their efficiency. The avoidance of turbulent conditions, exept perhaps at the inlet to promote flocculation, is essential. In the case of horizontal flow tanks broad inlet and overflow (outlet) weirs running the full width of the tank at each end are desirable to promote good distribution, laminar flow, efficient utilization of tank capacity and good sedimentation.

In the case of vertical flow tanks, liquor enters near the centre of the tank and about half way down, just above the sludge thickening zone. Flow is in an upward and outward direction towards take-off weirs at the surface. Under the influence of gravity, solids settle downwards against the flow, and are concentrated in the conical bottom section of the tank. Radial flow tanks are essentially circular versions of the horizontal flow tank. Liquor enters at a central distribution box and flows outwards towards a peripheral overflow weir. Settled sludge is scraped back spirally towards a central conical hopper by rotating submerged scrapers, and is removed via a central take-off pipe using the hydrostatic head.

II Mixing and Flow Balancing

Since the composition of the various tannery liquors fluctuates widely during the day, the effectiveness of sedimentation is very considerably enhanced if this is preceded by a mixing and balancing tank which permits the equalization of acid and alkaline liquors, and affords an opportunity for the co-precipitation reactions to occur between tannins in solution and any lime or soluble organic matters. In addition, liquors which may enter the balancing tank at varying rates of flow can be pumped to sedimentation tanks at a steady rate and, thus protected from surges in flow, the latters effectiveness is considerably improved.

The bulk of tannery liquors are discharged usually over a period of ten hours, but if the balance tank has sufficient capacity to contain one day's production of liquors, the subsequent stages of treatment can be operated over twenty-four hours, and consequently may be substantially reduced in size. A compromise in balancing may be to provide storage only for the segregated lime sulphide liquors (including the first wash liquor) so that these can be fed into the flow of other wastes which are discharged over a longer period and are predominantly acidic. Moreover if sulphide is to be removed (see later) two such tanks could be used alternately to treat and store the liquors, and then to dispense the treated liquor gradually during the following day.

It will, in individual cases, be desirable to assess the cost/benefit of limes only balancing, as compared with full flow balancing. A third scheme is provided (VIII C) "Full Flow Balanced" in which the provision of a full flow balancing tank permits appropriate reductions in subsequent plant size, and the elimination of peaks from the pattern of flow also leads to increased efficiency. In addition the operation of biological plant continuously over twenty-four hours is also preferable to its operation for ten hours followed by fourteen hours inactivity. Finally, mixing and balancing has the beneficial effect of diluting any toxic compounds which might otherwise pass through the unit as a plug dose at an inhibiting concentration.

III High Rate Biological Treatment

High rate biological filters provide a convenient means of removing a large proportion of the biologically oxidizable matter in a relatively small volume of plant [95], additionally, providing an effluent of intermediate quality, where such is acceptable for discharge, it provides a useful "roughing treatment" enabling reductions to be made in the sizes of subsequent biological treatment plants, where these are desirable to produce effluents of higher quality.

Contrary to widely held opinion, the packing medium used in high rate filters dos not necessarily need to be of the fabricated plastics construction now manufactured in Europe and the U.S.A. Indeed, unless floor space is so limited as to dictate the use of very tall towers, it is difficult to justify the use of fabricated plastics in place of a more conventional stone packing. [95] Biological filters filled with stones can achieve removals of 70% when loaded at rates as high as 2 kg of BOD/M^3 d. and as the construction of plastics packed towers cost fourfold the cost of stone filters, these would need to remove 70% of the BOD when loaded at rates as high as 8 kg/M^3 day in order to be competitive, which possibility seems unlikely.

The high rate filter consists, therefore, of a bed of stones packed in a tower up to 3 M in depth, the retaining walls of which may be constructed from any strong corrosion resistant materials which are conveniently to hand. Effective underdrainage is essential to permit egress of the percolated liquor and, just as important, the free access of air up the tower, as the process is aerobic.

Since biological filtration involves the conversion of dissolved organic matter into biological solids, a sedimentation tank is required to remove these before discharge of the liquor. Similar design considerations would apply to this tank as to those used for primary sedimentation. Although recirculation of effluent from the filter is to be used in operation of the filter (at a ratio of 1:1), and since sedimentation tanks are designed almost entirely on the basis of the hydraulic flow rate (except for activated sludge separation tanks where solids flux becomes important) it might be expected that a tank twice as big would be needed. However, this is not so as the humus solids will settle rapidly, and in any case very efficient removal of suspended matter is not important at this stage. Alternatively, it might in certain instances be preferable to recirculate unsettled filter effluent; and this would probably be quite acceptable in most cases.

IV Secondary Biological Treatment

When effluents of fairly high quality are required for discharge to clean rivers or other surface waters, further biological treatment at a much lower loading rate will be necessary. However, since the effluent has received pre-treatment in a high rate filter, the subsequent treatment plant can now be smaller than would otherwise have been the case. One or more conventional biological filters (structures similar to the high rate filter, but packed with 40-50 mm graded stones) loaded at the reduced rate of 0·1 kg BOD/M^3 d (as compared with 2·0 kg/M^3 d) could provide an effluent having the desired characteristics. However, this would occupy quite a lot of space, and in view of the need to reduce plant size to a minimum in urban areas, it is appropriate to consider the use of an activated sludge process which is much more economical in size. Basically the process consists in bringing the organically polluted water into contact with a very large concentration of aerobic bacteria and other micro-organisms present in the form of a flocculant biological agglomerate known as "activated sludge". The sludge floc is kept in intimate contact with the liquid phase by the same mechanism as is used to supply oxygen to the aerobic process. These are usually diffused air systems or mechanical surface aerators. In the process, in which the sludge floc is analogous to the biological slime in a biological filter system, a portion of the organic matter in the wastes is converted to more biological cellular material, whilst the remainder is utilised for energy, and converted to carbon dioxide and water. As with filters a sedimentation tank is needed to separate the activated sludge from the clarified effluent, but in this process the bulk (up to 75%) of the separated sludge is recycled to the beginning of the process.

Generally, the process tends to be less robust than biological filtration and more careful control is needed, but care has been taken in this report to use only relatively low sludge loading rates in calculating the recommended capacity of plant, and it is not envisaged that any insurmountable difficulties will arise if the plant is efficiently maintained. In any event, there is no simpler way of producing an effluent of high quality from a strong effluent in a restricted space.

V Tertiary Treatment

It seems most unlikely that an effluent of even better quality than that which would be produced by the foregoing processes would be necessary in the urban environment unless discharge is to a small stream used as a source of drinking water, or unless it is desired to treat and recycle a portion of the effluent for reuse within the tannery. However, for the sake of completeness, a process suitable for use in a restricted space is included.

Once again circumstances dictate process selection, and in urban areas it seems that only rapid gravity sand filters can be considered. These can of course be complicated by automation, but in the proposed scheme a simplified arrangement is indicated for backwashing the filter bed. If compressed air is to be used in the tannery the inclusion of an air scour capability would considerably facilitate the removal of entrapped solids during backwashing.

VI Sludge Disposal

The above treatment will result in the concentration of the solid fraction of the liquors in the form of a thin slurry. The disposal of this material is dealt with separately.

F Schemes for Use in Rural Areas

In rural, less densely populated areas, where the space available for effluent treatment will presumably be less restricted, it is possible to adopt a more "rustic" approach to effluent treatment; a truly hole-in-the ground policy, but supplemented by twentieth century technology where appropriate (i.e. economic or sensible).

I. Primary Treatment - Sedimentation

Where it is feasible to construct lagoons having a capacity to hold one whole days flow of effluent, the functions of mixing, flow balancing, sedimentation, sludge concentration and sludge storage can be achieved in one stage. In fact the "stage" consists of two lagoons connected in series, which permits the primary lagoon to become somewhat inefficient, as it fills with sludge and loses effective capacity, since the effluent always receives a subsequent settlement in the second lagoon. Because it will be necessary to remove the primary lagoon regularly from service, three lagoons should, ideally, be provided and be operated as follows:-

Schedule of Operating Sedimentation Lagoons

Period:	Primary Lagoon	Secondary Lagoon	Thickening & Desludging
1	A	B	-
2	B	C	A
3	A	C	B
4	A	B	C

It will be seen that the lagoons are not operated in strict rotation owing to the difficulties associated with transferring liquors from lagoon C to lagoon A if the former were to be used as a primary lagoon. Normally, liquors would flow by gravity from one lagoon to another via open channels, and simple earth dams or wooden planks would be used to route the liquors.

The lagoons would be desludged by re-routing the liquors in accordance with the Table above with a frequency determined by experience. Before desludging the lagoon could be permitted to stand for a period to allow the sludge to settle and thicken up, and during this time, any supernatant water would be decanted or pumped from the surface of the lagoon. Later the sludge could be removed by a portable diaphragm type sludge pump to a suitable area of drying beds or to tankers for transport and disposal at some remote area.

II Anaerobic Lagoon

Any benefit derived by anaerobic lagooning in European effluent treatment tends to be accidental rather than by design, as lagoons used principally for sedimentation naturally become anaerobic.

[illegible] ... with anaerobic organisms [illegible] red [illegible] effluents from 1,[illegible] [illegible] ten [illegible] lagoon under anaerobic [illegible]

In this [illegible] values [illegible] in excess of 1,[illegible] mg/l are expected and Sa[illegible]'s data has been used only to estimate the quality of effluent which may be expected after retaining the effluents [illegible] for a period of ten days in such a lagoon. However, the primary treatment given will reduce the rate of "washout" of micro-organisms, so that slightly improved performance might be expected. It would also be beneficial if, in this stage, arrangements could be made for liquors to enter this tank at its base by means of [illegible] pipe to reduce surface agitation, and enable the formation of a protective crust of solids on the surface of the lagoon. The bottom inlet would also promote good solids contact in the lagoon, and to further assist this, the lagoon has been made deep and narrow in relation to its length. Good mixing with anaerobic sludge at the inlet end would be beneficial, and a potential improvement at some future time might be to pump sludge from the outlet end of the deep lagoon back to the inlet to mix with the inflowing liquors.

III Aerobic Treatment - Oxidation Ditch

The effluent would probably be suitable for discharge to foul sewers after treatment in the primary and secondary sedimentation lagoons, but further treatment in the anaerobic lagoon (II above) would reduce the load to be treated at the sewage works, and consequently would lower the charges levied for its discharge. However, foul sewers for conveying effluents to sewage works are generally less available in rural areas, and if the effluent has therefore to be discharged to a clean river or surface water, some form of aerobic biological treatment will be necessary. This is most conveniently given in some form of aerobic lagoon, but to be truly effective, without occupying vast areas of land, it is essential to maintain a higher population of micro-organisms than would result if the normal rate of "washout" were permitted to control the process. The higher population is achieved by removing those present in the effluent from the lagoon and returning them to mix with more liquor entering the lagoon, as in fact, is the practice in operating the activated sludge process described earlier, and which this process aims to emulate in a simplified way.

In order to ensure conditions whereby the increased population of micro-organisms can operate effectively it also becomes necessary to supply oxygen to the lagoon artifically, using mechanical aerators, of which several designs are commercially available.

A very convenient and simple concept for bringing these conditions about is embodied in the "oxidation ditch". This is essentially an annular tank of trapezoidal cross section around which the effluent is circulated by steel brush type rotating aerators which also serve to resuspend the active sludge floc and aerate the liquor. Waste liquors enter the "ditch" continuously, and after a period of residence, which can be up to two to three days for domestic sewage, the "mixed liquors" leave the ditch when the activated sludge floc is separated in a suitable sedimentation tank and recycled to the ditch whilst the clarified effluent is discharged. Such systems are used successfully for small rural and some industrial installations in developed countries, and one in Holland has been operated on tannery effluents in a pilot scale by Eggink and Kagei (97).

The oxidation ditch is extremely simple, low in cost, almost maintenance free and, when properly commissioned, is capable of producing effluents of exceptionally high quality.

In modifying the mode of operation of the ditch it is possible to dispense with the final sludge separation tank. This involves temporarily stopping the aeration rotors, and the waste feed to the ditch, two or three times a day so that the mixed liquor stops circulating, and the activated sludge floc settles out. As soon as an appropriate depth of supernatant liquor has been formed effluent water is decanted from the ditch by lowering the level of an adjustable weir over which the clear portion of the water flows to waste. The decanting operation may last for 0·5 to 1·0 hours, and after a sufficient quantity of liquid has been discharged, the rotors are restarted and normal operation is resumed.

As with the activated sludge system, it is necessary occasionally to remove a portion of the activated sludge which gradually increases in concentration as a result of biological growth.

It will be obvious from the foregoing that the oxidation ditch is essentially a variation of the activated sludge process but the plant design, as well as being simple and not necessarily requiring a final sedimentation tank, is much more robust and stable, by virtue of its very long retention time, and therefore its sludge loading rate - i.e. kg of BOD/kg of activated sludge solids per day. (Usually expressed as kg BOD/kg MLSS d^{-1} where MLSS = mixed liquor suspended solids.)

The considerable dilution of liquor entering the ditch also affords some protection from the effect of shock loads of toxic materials or peaks in the concentration of BOD and flow. Moreover, the very low BOD loading and the long time for which the sludge solids are retained in the ditch, up to one-hundred days, means that more sludge is "burnt up" (biologically) by the endogenous respiration of the bacterial mass. This leads to a more "mineralized" sludge which is less malodorous and easier to dewater. A further useful consequence of the lower rate of loading is the substantially reduced quantity of sludge produced, 0·3 kg of sludge solids/kg of BOD removed, as compared with about 1·0 kg/kg of BOD removed for a conventional activated sludge plant.

IV Tertiary Treatment

An effluent of exceptionally high quality may be expected from the oxidation ditch if constructed and operated within the terms set out in this report. In fact the ditch capacity recommended is sized so as to permit operation at an increased flow or load if an effluent of reduced standard is acceptable. In the event of it being necessary to discharge the effluent to a water course used eventually as a source of drinking water, some slight further improvement may be achieved by a tertiary "polishing" stage. It may also be useful to provide a buffer zone to protect against temporary malfunction of the plant.

Irrigation of secondary effluent over grassland has been used successfully at many works in England[98] as a means of final polishing. In this method effluent is run onto land through a system of irrigation channels, flows over the surface, and is collected by a second series of channels or flows directly away to a stream. The land must be fairly well graded, and should not slope so steeply that channeling is encouraged; it has been recommended that this gradient should not be more than 1 in 60. The method for preparing land for grassland treatment has been well described by Daviss [99]. With plots which are specially prepared it is usual to sow a special mixture of deep rooted grasses (for example, S37 Cocksfoot - Dactplis glomerata - at about 30 lb/acre);

it appears, however, that in a few years the natural flora is restored, and plots at which no attempt at seeding has been made give satisfactory results. It is not necessary to keep the grass short, but occasional cutting is required to prevent the growth of rank weeds. It is therefore convenient to divide the land into two or three plots, so that each in turn may be allowed to dry out before cutting. Periodically the plots must be cleared and accumulated solids removed. A report by Truesdale (98) on operation of grass plots at three works in England indicates average removals of 61-76% of the suspended matter, and 55-57% of the BOD from humus tank effluent after biological filtration.

V Miscellaneous Notes

A. The various types of sedimentation tanks, for use in urban schemes, are discussed earlier in these notes. It may be pointed out, however, that since vertical flow tanks are necessary for the separation of activated sludge, owing to the need to continuously recycle the settled activated sludge, it may be economic to construct all the sedimentation tanks to this standard design so that the same design plans and concrete shuttering (if applicable) could then be used.

Generally similar tank sizes are used in the individual schemes, except for the humus tank of the urban scheme, which has to accept a substantially increased flow of recirculated high rate filter effluent.

B. A considerable quantity of earth spoil will be removed when excavating holes for the rural schemes. The full exploitation of this spoil will depend on ground conditions such as the land gradient and the water table.

If some pumping from the tannery is possible (or necessary) the entire sedimentation lagoons might be formed above datum by raising banks using earth removed from the anaerobic lagoon and the oxidation ditch.

Alternatively all holes could be excavated so that each water line is at datum, and spoil used simply to provide the freeboard.

C. In view of the shallow slope (45°) of the holes used in the rural schemes, it seems unlikely that, except in extreme cases, there will be any necessity to "line" the sedimentation or anaerobic lagoons. However, the oxidation ditch will probably need lining around the curved sections and in the proximity of the aeration rotors. It may also, in some instances, need lining along its entire length.

The selection of lining material will be governed by what is locally available; bricks, stones, slates or paving slabs might all be used. Butyl rubber sheeting has also been used in Europe. However, the lining must be heavier than water, otherwise floatation will occur.

CHAPTER VIII

CHROME TANNERY EFFLUENT TREATMENT SCHEME

General Specification:

Production: 1,200 hides/day to chrome side upper leather (ID/WG.157/11)

Effluents: Volume 260 m^3/d

BOD 3600 mg/l

Suspended solids 10,000 mg/l

	RURAL	URBAN
Treatment:	1. Primary Sedimentation (incorporating mixing and balancing)	1. Mixing and balancing
	2. Anaerobic lagoon	2. Primary sedimentation
	3. Oxidation ditch	3. High rate biological filtration
	4. Grass plots	4. Activated sludge treatment
		5. Rapid gravity filters.

A. Chrome Tannery Effluent - Scheme for Rural Areas

1. Primary Sedimentation

Three earth lagoons, any two of which can be connected in series as primary and secondary lagoons - see Introductory Notes, Chapter VII, F.2

Dimensions of each lagoon

Volume = 260 M^3 excluding freeboard

Dimensions: 13 m long x 10 m wide x 2·5 m deep

This allows 0·5 m for freeboard. The lagoons should be dug with 45^o sloped sides which should not require lining. Part of the deptch may be obtained using spoil.

Effluent from sedimentation lagoons:-

Two days retention in the two combined tanks should produce reductions as follows :-

BOD reduction by 25% = 2700 mg/l

Suspended solids reduction by 60% = 4000 mg/l

II Anaerobic Lagoon

Assuming an input of similar quality to that leaving the sedimentation lagoons, and using the data obtained by Sastry to estimate their likely performance, the dimensions of and effluent from the anaerobic lagoon are suggested as follows :-

Dimensions: 50 m long x 15 m wide x 5·5 m deep
(i.e. 5·2 m plus 0·3 m freeboard)

The dimensions may be regarded as approximate and the sides should be sloped as dictated by the ground conditions. The inlet should be submerged as suggested earlier.

Effluent: (estimated from the experience of Sastry (25))
BOD reduction by 50-60% = 600 mg/l
Suspended solids reduction by 75% = 1000 mg/l

III Oxidation ditch

In view of the preceding anaerobic treatment only two days retention should be sufficient for the oxidation ditch. This would involve a working capacity of 520 m^3 in the form of a closed circuit trapezoidal channel. The 1 m deep channel width is 4 m at the top and 2 m at the base with 45° sloped sides. The total circuit length needs to be 170 m., viz:

75 m long parallel trapezoidal channels separated by a 2 m wide island and connected at each end by 5 m maximum radius semi-circular trapezoidal channels. The wider dimension of the channel is at waterline level and the freeboard of the ditch is to be provided using the spoil (earth) removed by the excavation.

(a) Check on sludge loading:

As a further check on the predicted performance of the oxidation ditch it is possible to calculate the BOD:sludge solids loading rate, L, assuming a fairly easily maintained mixed liquor suspended solids content of 6000 mg/l or 6 kg/m^3.

Total daily BOD load entering the ditch (@ BOD = 600 mg/l)
= 260 m^3 x 0·6 g/l = 156 kg BOD/day.

Total mass of activated sludge solids in system
= 520 m^3 x 6·0 g/l = 3120 kg

$$\text{Therefore } L = \frac{156}{3120} = 0{\cdot}05 \text{ kg BOD/kg MLSS/day}$$

Thus the sludge loading rate is sufficiently low to produce an effluent of good quality.

(b) Disposal of Final Effluent

In order to avoid the need for a separate final sedimentation tank, the ditch should be operated on a "Store and Decant" principle. This necessitates stopping the rotors at 06.00 h. 09.00 h., 12.00 h and 15.00 h. on working days, allowing the floc to settle, and then lowering an adjustable weir and discharging a sufficient volume (i.e. [illegible] m^3) of water to permit the ditch to accommodate the appropriate quantity of incoming liquors before the next decanting period. This means lowering the level of mixed liquors in the ditch by some 100 mm. If the surface aeration brush rotors are at a fixed height this should be so arranged that the average depth of immersion is 120 mm so that the true depth varies between 70 and 170 mm.

(c) Aeration Rotors

The aeration rotors consist of cylindrical brushes with steel spines, and are the subject of patents held by the T.N.O. Institute in Holland who issue licences for manufacture to various firms.

The power required to drive the aerators depends on the oxygen requirements, but for the scheme described, the installed water capacity will most probably be dictated by the need to keep floc in suspension rather than the oxygen requirement.

It is suggested that 4 five foot rotors are installed. This will involve a total installed horse power of 12 h.p. and each consume 32 Kwh/day.

IV Grass Plots

Satisfactory results are reported by Truesdale [98] to be obtained when grass plots were irrigated with sewage effluent at the rate of 32 l/m^2h. If effluent from the ditch is irrigated over ten hours only each day this is 26 m^3/h, therefore a grass plot area of very approximately 800 m^2 is required, and so a plot 30 m x 30 m should be sufficient.

See Figs. I and II overleaf for diagrammatic outline of treatment suggested.

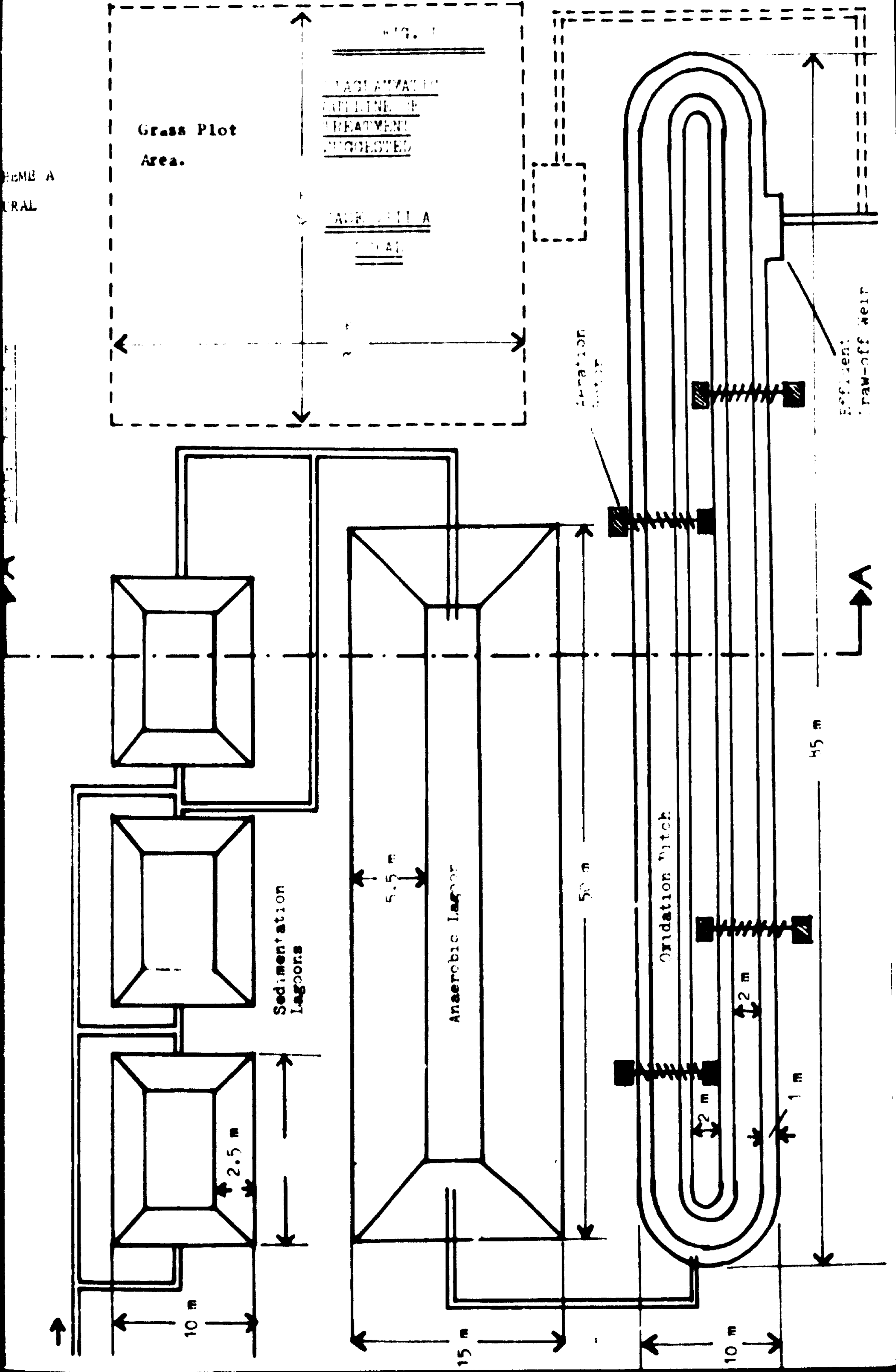
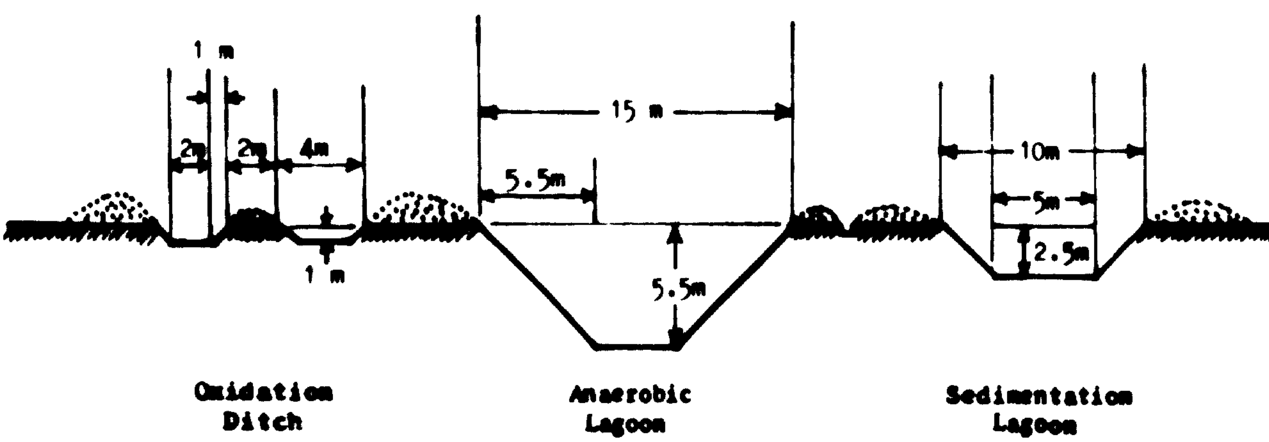

Grass Plot
Area.
Sedimentation
Lagoons
Anaerobic Lagoon
Oxidation Ditch
10 m
15 m
50 m
5.5 m
2.5 m
2 m
1 m
10 m
85 m

FIG. II

SECTION OF TREATMENT PLANT RELATING TO CASE VIII A - RURAL

SCALE: 3 mm = 1 m



Section through A............A

8 Chrome Tannery Effluent - Scheme for Urban Areas -- Limes Balancing Only

I Mixing and Flow Balancing

This scheme is designed using flow balancing of the highly alkaline limes and lime washes only. It is assumed that these will amount to about 25% of the total flow.

Hence capacity of balancing tank = 65 M^3, so that allowing for freeboard 4 m x 4 m x 5 m deep would be adequate. Mechanized mixing would be desirable as sedimentation here is undesirable, but hand plunging and bottom draw off would perhaps suffice. Two similar tanks should be provided for alternate use as sulphide oxidation tank and lime dosing tank. (The former process is described later).

II Sedimentation

Either vertical flow or horizontal flow tanks can be used for primary sedimentation (see Annex XIV. - Fig. I). Vertical flow tanks are more economical on ground space and will in any case be needed for sludge separation in the subsequent activated sludge treatment stage. Dimensions for horizontal flow tanks are, however, supplied.

(a) Vertical Flow Tanks

These are usually designed on upward flow velocities which should be such as to permit a nett downward movement of suspended matter.

If flow is from 07.00 h. to 17.00 h. = 10 h. then flow rate

$$= \frac{260 \ M^3}{10 \ h} = 26 \ m^3/h.$$

If we allow a 0·5 m/h upflow rate we need 52 m^2 tank area - preferably split into two tanks, each of 26 m^2 which is about 5 m x 5 m, with an effective depth of 2 m and a sludge collection/thickening hopper of appropriate depth to provide a 60° slope.

(b) Horizontal Flow Tanks

These are based nominally on retention time and for tannery wastes 6 h. should be provided.

Therefore capacity of tanks should be 26 m^3/h x 6 h = 156 m^3, preferably split between twin 2 m deep tanks of 80 m^3 each. Therefore surface area for each tank = 40 m^2. The relative dimensions are important and a suitable size would be 4 m wide x 10 m long.

A 1 in 10 slope is suitable for sludge removal in an "empty" tank therefore the depth should slope from 3 m at the inlet to 2 m at the outlet end.

NOTE. Since one tank will always be out of service whilst desludging THREE TANKS will be needed.

The linear flow velocity along these tanks will be $\frac{13\ m^3}{8\ m^2}$ m/h = 1·6 m/h = 27 mm/min., which is a further check that effective sedimentation will be achieved.

III High Rate Biological Filtration

The primary treatment of mixing, partial balancing and sedimentation should reduce the BOD and suspended solids as follows :

BOD, 3600 mg/l reduced by 25% to 2700 mg/l

Suspended solids, 10,000 mg/l reduced by a least 60% to 4000 mg/l. The high rate filter (see note E III - Chapter VII) should be a tower packed with 100 mm to 130 mm graded stones or crushed rock to a depth of 3 m (depth is governed by the strength of the retaining walls). The filter could be loaded at a rate of 2 kg of BOD/m^3 day, and would then remove at least 70% of the applied BOD.

The total daily BOD load = 260 m^3 x 2·7 kg/m^3 = 700 kg of BOD/day.

However, without full flow balancing this load will be applied in 10 h equivalent to a virtual daily rate of 2·4 x 700 = 1680 kg/d.

At 2 kg/m^3d we would need 840 m^3 of medium and at a maximum depth of 3 m the area is 280 m^2 or about 17 m x 17 m square. This will result in a superficial hydraulic loading rate of about 0·1 m^3/m^2h, and in order to ensure adequate wetting of the filter medium, and to dilute the very strong liquors, it will be essential to recirculate filtered effluent at a ratio of at least 4 to 1 and therefore a pump of capacity up to 120 m^3/h should be provided.

The filter must also be provided with a suitable means of distributing the liquor on to the top of the bed. Ideally a travelling distributor would be provided but fixed, upward pointing, jets or a series of V-notched channels may suffice. It is equally important that good underdrainage is provided in the form of spaced drainage tiles, or very carefully placed bricks on a sloped concrete base.

Humus solids produced in the filter will emerge in the filter effluent and these must be removed in sedimentation tanks similar in design to those used for primary sedimentation (see figs. in Annex). Perfect settlement is not required, and the rapidly settleable solids should make the increased flow acceptable.

IV Activated Sludge Treatment

This process has been selected for reasons stated in [illegible] Chapter VII & IV. The design size of this stage is based on the [illegible] and [illegible] mixed liquor suspended solids content. In order to promote satisfactory operation in the possible absence of skilled supervision a design loading rate of only 0·15 kg of BOD/kg of MLSS per day has been selected.

The high rate filter is expected to reduce the BOD of the waste liquors by 70% i.e. from 2700 mg/l to 800 mg/l.

The total load entering the activated sludge plant = 250 m^3 x 0·84 kg/m^3 = 210 kg/d. However, this will be fed to the plant during only 10 h. which is equivalent to a virtual daily load of 210 x 2·4 = 500 kg.

At a sludge loading rate of 0·15 kg BOD/kg MLSS we shall need 3300 kg of mixed liquor suspended solids (MLSS) in the system.

The maximum concentration of mixed liquor suspended solids which can be carried in the system depends on the size and efficiency of the final sedimentation tanks. Since the settled activated sludge must be returned to the aeration tank continuously it is essential here to use vertical flow or mechanically scraped radial flow tanks. If vertical flow tanks exactly similar to those used in the two previous stages are used (the most economical arrangement) it is likely that concentrations of activated sludge solids up to 300 mg/l could be separated.

3300 kg of MLSS are required, and at the above concentration of 3 kg/m^3 this requires a total tank capacity of 1100 m^3.

If the tank is 3 m deep this is 370 m^2. This might conveniently be contained in four aeration tanks connected in series, each measuring 10 m x 10 m in plan (this allows some essential freeboard).

The tanks must of course be aerated by either diffused air or mechanical surface aerators. The latter provide the simplest and most trouble free operation for a small plant and are commercially available in many countries, but not always in developing countries.

As already mentioned, provision must be made to separate the activated sludge from the final effluent. This can be achieved in tanks of exactly similar size and design to the vertical flow tanks suggested for primary sedimentation. Hence if concrete is used one set of shuttering can be used to construct all six sedimentation tanks which will permit considerable economies in capital cost. Sludge must be returned to the aeration tank at a rate equivalent to the flow of effluent, i.e. 25 m^3/h and an appropriately sized pump be provided.

V Rapid Gravity Filters

The reasons for selecting this process in the very unlikely event of further treatment being required are set out in note in Chapter VII.E. They are designed entirely on hydraulic flow rates - in the present case 25 m^3/h. About 5 m^3/m^{2}h is recommended.

We should therefore require 5 m^2 of filter area. Basically the filter consists of a 0·5 m deep bed of 1 mm graded sand supported on a 0·2 m deep bed of 20 - 30 mm gravel covering perforated drainage pipes, perforated with 10 mm holes on the sides and underneath. Secondary effluent is fed onto the sand bed to a depth of up to 2 m and filters through the bed to be drawn off through the drain pipes. The rate of draw off is controlled by an outlet valve which is gradually opened as resistance develops in the filter. When the flow falls to a low level under the full 2 m head of water pressure, the filter is backwashed by pumping filtered effluent through the drainage pipes. Sometimes an air scour is used to loosen the entrapped solids, by alternately passing compressed air through the drainage pipes.

Backwash water containing high suspended solids is recycled to the activated sludge stage inlet. Two such filters will be required to permit continuous operation whilst one or other filter is undergoing backwashing.

See overleaf Figs. III and IV for diagrammatic outlines of treatment suggested.

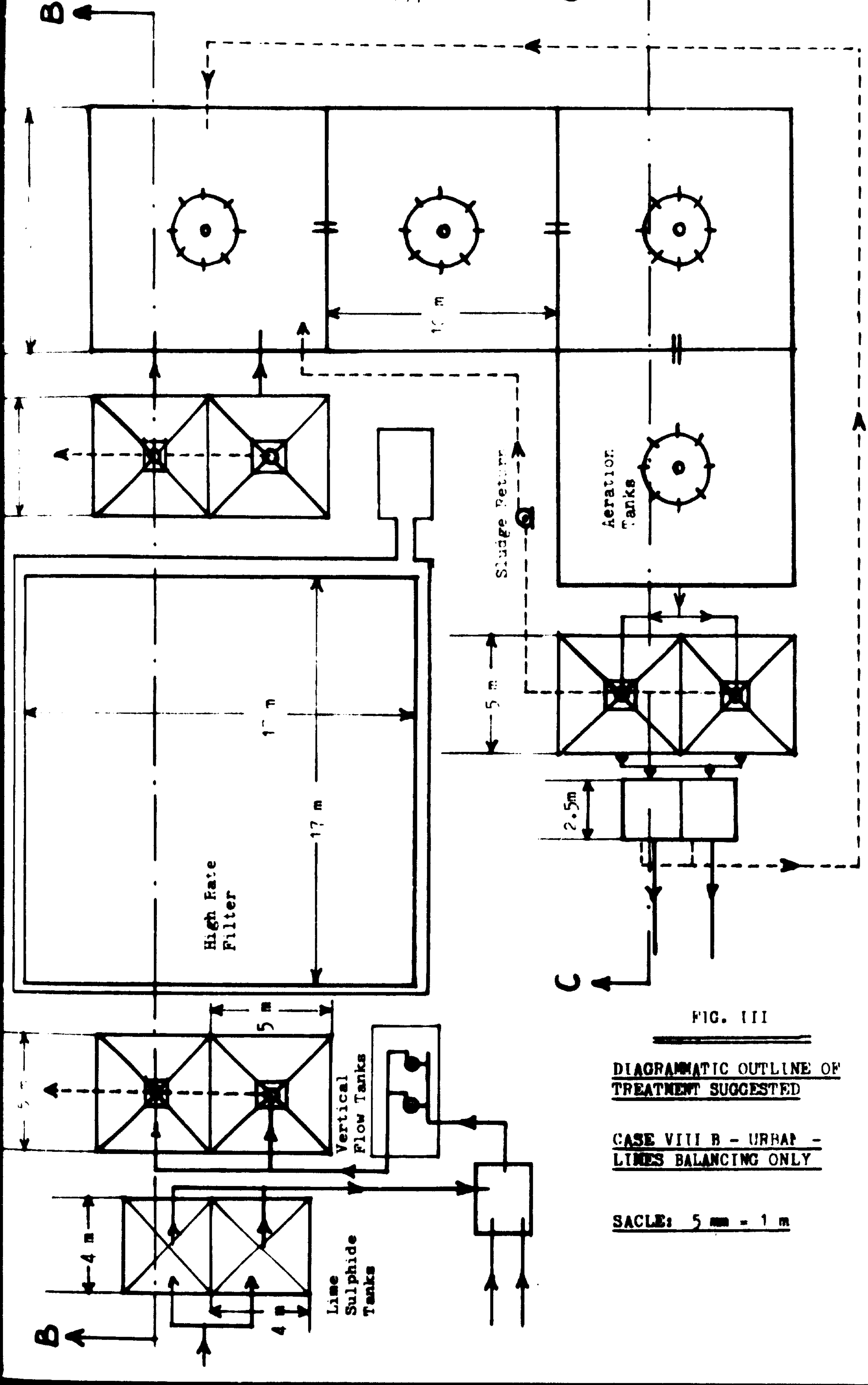


FIG. III

DIAGRAMMATIC OUTLINE OF TREATMENT SUGGESTED

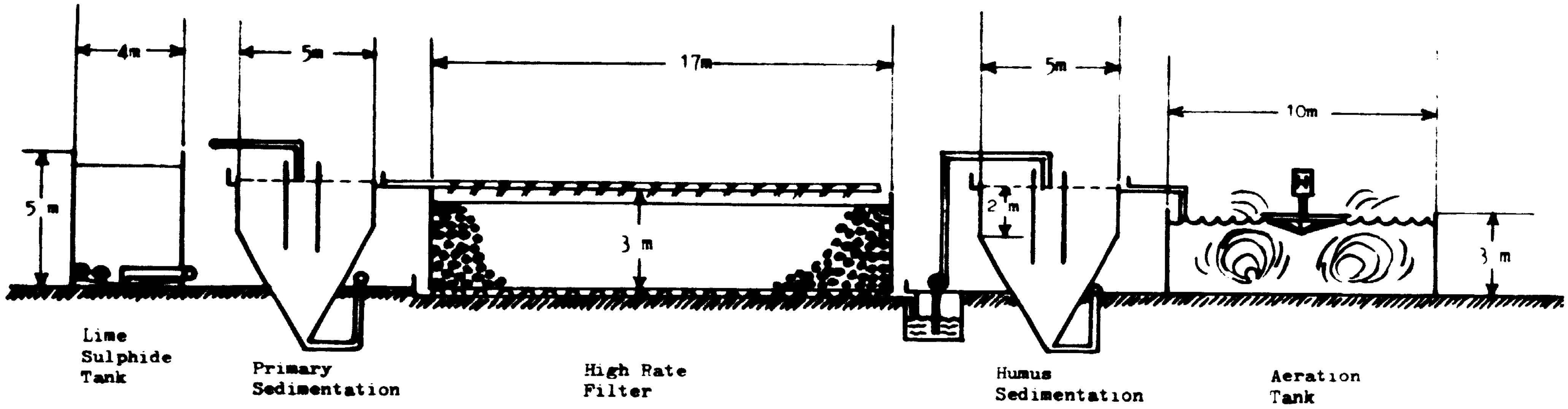
CASE VIII B - URBAN - LIMES BALANCING ONLY

SACLE: 5 mm = 1 m

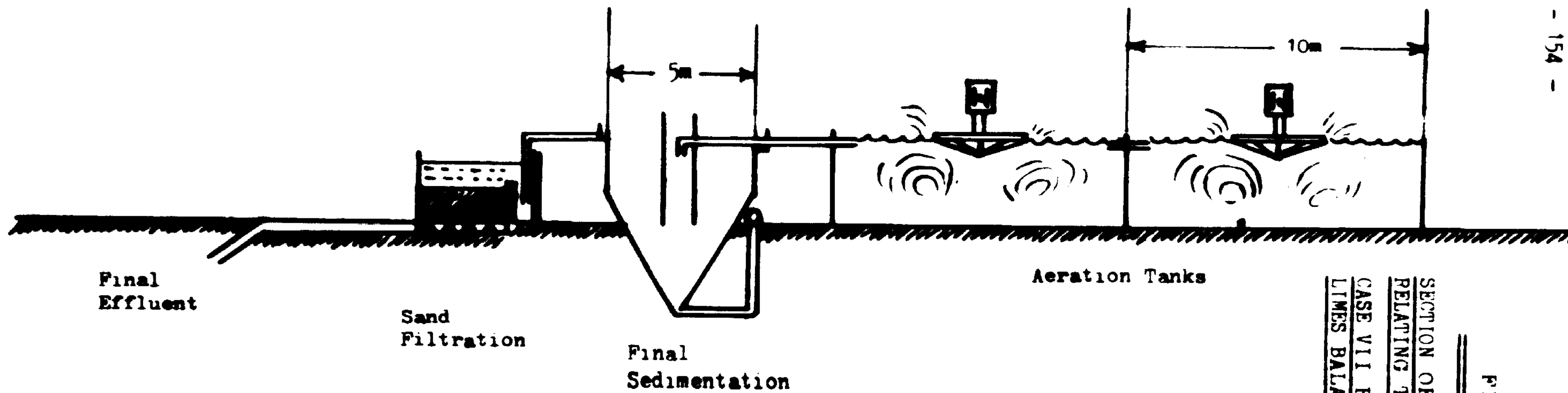
FIG. IV

SECTION OF TREATMENT PLA[NT]
RELATING TO:

CASE VII B - URBAN -
LIMES BALANCING ONLY



SECTION THROUGH B - - - - - - - B



SECTION THROUGH C - - - - - - - C

SCALE: 5 mm = 1 m

C. Chrome Tannery Effluent - Scheme for Urban Area - Full Flow Balancing

In the scheme [illegible] the lime liquors were separated and fed into the main [illegible] gradually purely to [illegible] maximum equalization of the pH. All the effluent produced during processing in the absence of a balancing tank had to be treated during ten hours. If a balancing and mixing tank is installed and the contents pumped out for treatment over twenty-four hours the subsequent plant can be reduced in size - and will operate more efficiently under steady flow conditions.

1. Mixing and [illegible] Balancing

This must hold one whole days flow of liquors - 250 m^3. The balancing tank size should be 10 m x 10 m x 3 m deep. Sedimentation is undesirable in this tank and gentle agitation by slow large bladed stirrers or by frequent hand plunging is necessary. A central bottom take off pipe is also desirable. Forward pumping rate = 11 m^3/h.

II Sedimentation

a) Vertical flow tanks

Flow is now over 24 h.

$$\text{Rate} = \frac{250\ m^3}{24} = 11\ m^3/h.$$

Allowing a 0·6 m/h upflow rate 18 m^2 of tank area is required, i.e. two tanks each of 9 m^2 area. Hence tanks should be 3 m x 3 m x 2 m effective depth with an appropriate 60^{o} sloped sludge hopper.

b) Horizontal Flow Tanks

With 6 h retention at 11 m^3/h volume of tank = 66 m^3 in two tanks each of 33 m^3 and with 2 m effective depth = 16·5 m^2 in area, i.e. 3 m wide x 5·5 m long. The tank bottom should slope from 2·5 m at the inlet to 2 m at the outlet end.

Three such tanks will be required (one being desludged).

III High Rate Biological Filtration

Daily BOD load is still 700 kg but this is now spread over 24 h. Loaded at 2 kg BOD/m^3d the requirement is 350 m^3 of filter medium. At a maximum depth of 3 m the filter area needs to be 120 m^2.

High rate filter needs to be 10 m x 12 m x 3 m deep, arranged as described previously.

Pump capacity of 50 m^3/h will be required for feed and recirculated liquors.

Humus solids may be removed in tanks of similar design to those used for primary treatment.

IV Activated Sludge Treatment

Following the high rate treatment the total BOD load remaining to be dealt with by the activated sludge stage will be 210 kg of BOD/day over 24 hours.

At a sludge loading of 0·15 kg BOD/kg MLSS/d the requirement will be 1300 kg of mixed liquor suspended solids (MSLL) in the system. If the acceptable concentration of MLSS is 3000 mg/l the requirement is an aeration tank capacity of $\frac{1400}{3}$ = approximately 470 m^3. If the tank is 3 m deep this must be 160 m^2 in area. This will conveniently be contained in two aeration tanks connected in series, each measuring 10 x 8·5 m in plan (allowing 0·5 of freeboard).

The vertical flow tanks used to separate the activated sludge from the final effluent can be exactly similar in size and design to those used for primary treatment, but they must be vertical flow tanks, to permit continuous sludge return.

Sludge should be returned to the aeration tank at a rate equivalent to the flow of effluent, i.e. 11 m^3/h and a pump of the appropriate rating should be provided.

V Rapid Gravity Filter

To treat a flow of 11 m^3/h at a design rate of 5 m^3/m^2h the requirement is 2 m^2 of filter area constructed and operated as described in the previous scheme.

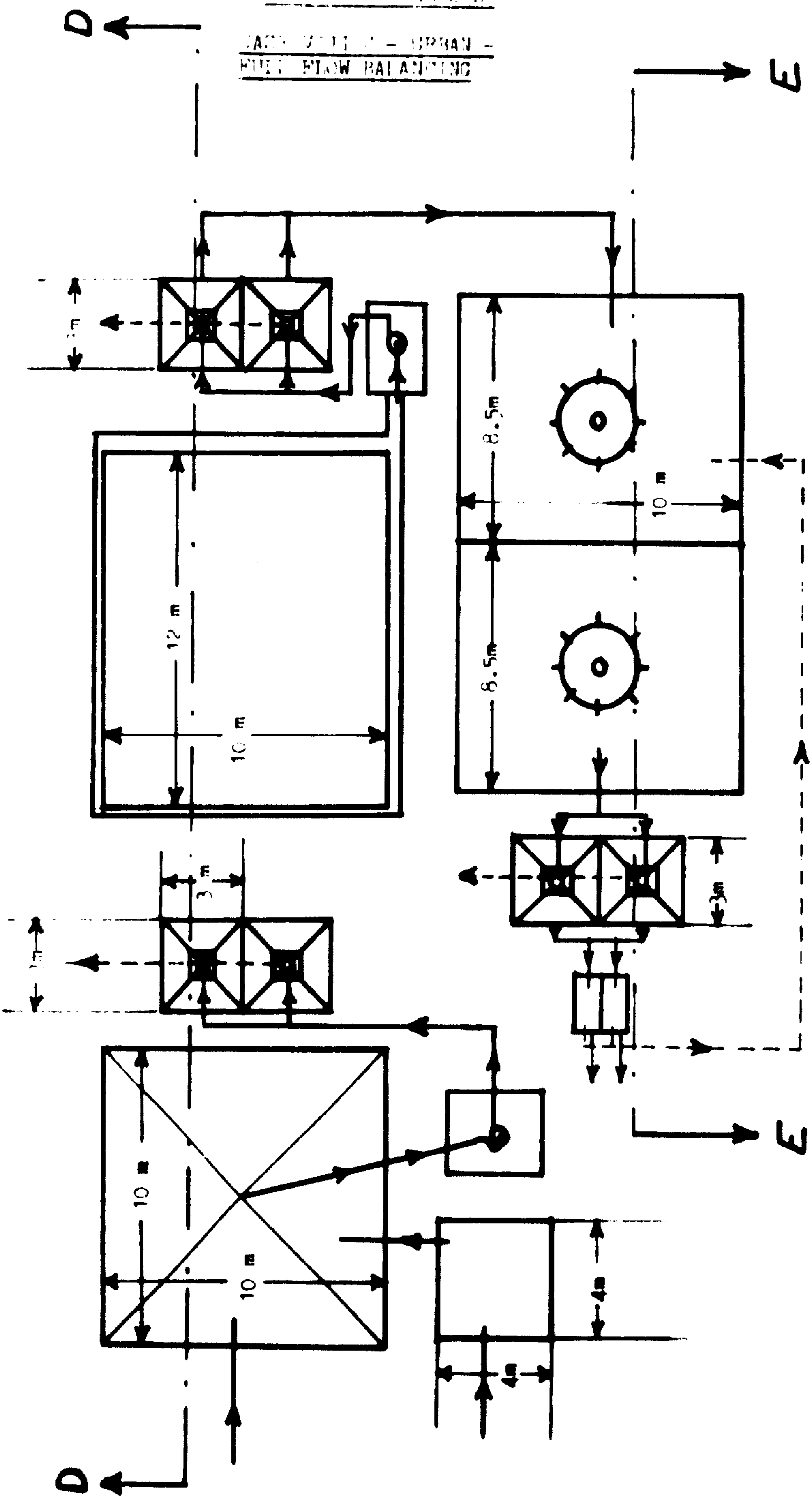
Two filters will be required, as before, to permit continuity of operation.

See overleaf Figs. V and VI for diagrammatic outline of treatment suggested.

FIG. V

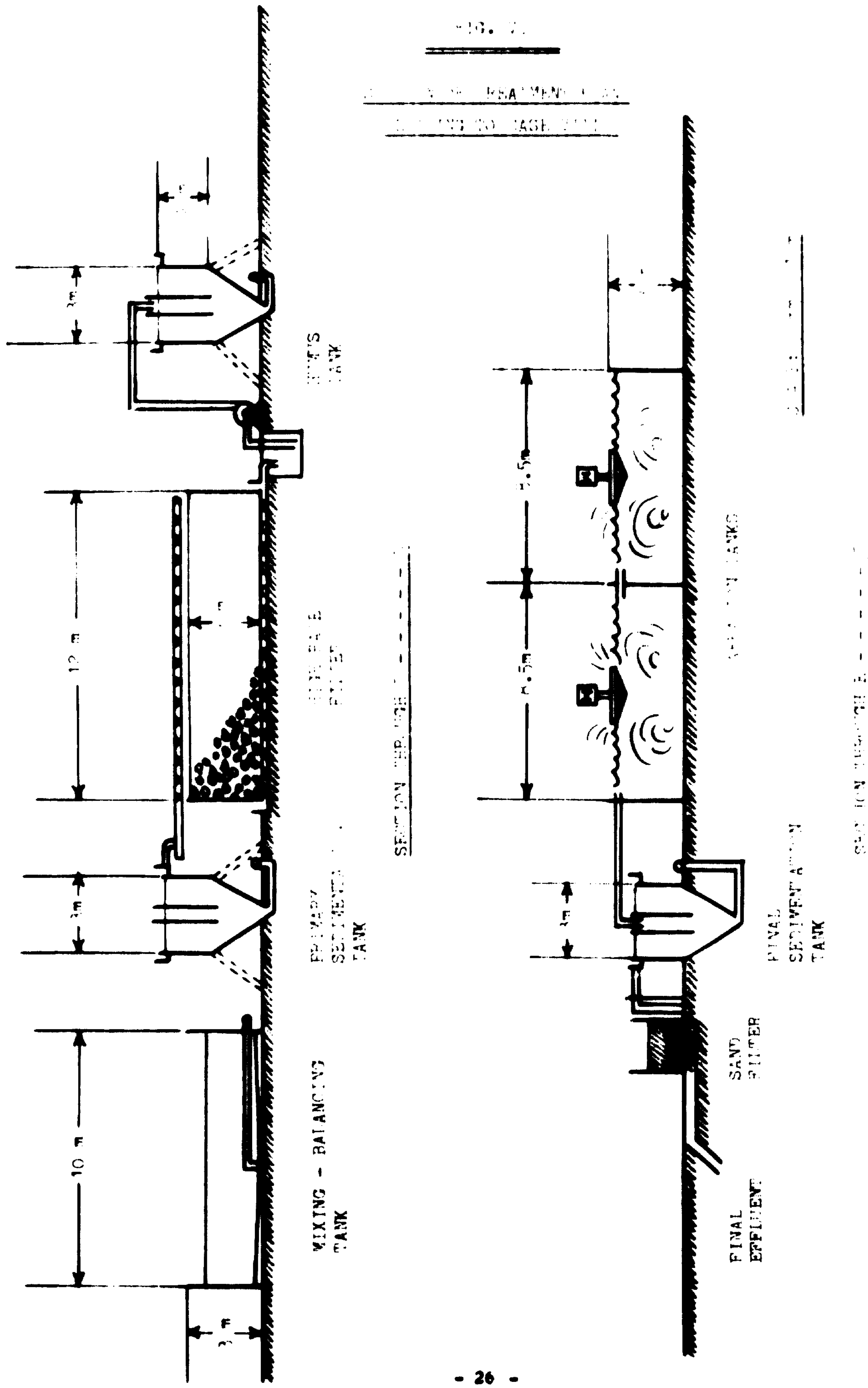
DIAGRAMMATIC OUTLINE OF TREATMENT SUGGESTED

CASE [illegible] - URBAN - FULL FLOW BALANCING



SCALE: 5 mm = 1 m

FIG. 7.



10 m
3m
12 m
MIXING - BALANCING TANK
PRIMARY
TANK
SAND
FINAL
TANK

D. Chrome Tannery Effluent - Sludge

I. Sludge Production (from complete treatment)

(Applicable to Schemes VIII A, B and C - See Also Chapter X A)

- From suspended solids :

  260 m^3/d at 10,000 mg/l = 2600 kg of dry solids/day

- From BOD removed :

  (assuming 35% of the BOD is attributable to suspended solids)

  BOD after primary sedimentation = 2700 mg/l

  2700 x 65% = 1700 mg/l

Therefore sludge production = 260 m^3/d x 1·7 x 0·8

= 350 kg of dry solids/day

2600 + 350 = approx. 3000 kg/d

If sludge is thickened to 5% solids content there will be 60 m^3 of sludge/day.

(Treatment after high rate filter or anaerobic lagoon would produce about 56 m^3/d. Primary treatment alone would result in about 42 m^3/d).

II. Area of Drying Beds Required

60 m^3/day of wet sludge placed on beds to a depth of 0·5 m requires a bed area of 120 m^2.

Suggested bed: 12 m long x 10 m wide

If the drying period in a dry climate = 2 weeks and if 5 day working is practised, 10 such beds will be required covering an area of 12 m x 100 m.

III Size of Filter Press Required

60 m^3/d of sludge containing 5% of dry solids i.e. 300 kg/d of dry solids pressed into cakes contained 40% of dry matter.

Volume of press cake would be 7·5 m^3.

(This is ignoring the higher density of the cake solids; if this is taken as being 2·0 the volume of press cake would be only 6 m^3/d. However, since the density of the sludge solids is unknown, but certainly not less than 1·0, the figure of 7·5 m^3 of cake is used in calculating filter press capacity).

Generally chrome tannery sludge is not difficult to filter press and certainly if some chemical conditioning of the sludge is available, it should be possible to form press cakes 5 cm thick using 1 m^2 press chambers and a 5 hour pressing cycle. Hence 20 chambers will produce 1 m^3 of press cake. Therefore the recommended filter press requirements are :

Two 40 chamber filter presses (5 cm chambers). This will produce 4 m^3 of press cake per pressing cycle. Two cycles/day will produce 8 m^3/day. Two presses should be installed as in the event of a breakdown a single press could cope by operating overnight and at weekends.

CHAPTER [illegible]

VEGETABLE SOLE LEATHER TANNERY - EFFLUENT

General Specification:

Production: [illegible] hides/day of vegetable sole leather (ID/WG.[illegible]/9)

Effluents: Volume 60 m^3/d

BOD 5100 mg/l

Suspended solids 4500 mg/l

Treatment:

RURAL	URBAN
1. Primary sedimentation	1. Mixing and balancing
2. Anaerobic lagoon	2. Primary sedimentation
3. Oxidation ditch	3. High rate biological treatment
4. Grass plots	4. Activated sludge treatment
	5. Rapid gravity filters

A. Veg. Tannery Effluent - Scheme for Rural Areas.

The design calculations only are given in dealing with vegetable tannery effluent. The philosophy of process selection and plant design and operation is similar to that applying in Chapter VIII - Chrome Tannery Effluent where these factors are described in detail and to which reference should be made as appropriate.

1. Primary Sedimentation

Three sedimentation lagoons of nominally one days capacity each 60 m^3.

Suggested dimensions 6 m x 5 m x 2·5 m deep with 45° sloped sides and interconnected. Sedimentation can be expected to reduce the BOD and suspended solids as follows :-

BOD 5100 mg/l reduced by 20% to 4080 mg/l

Suspended solids 4500 mg/l reduced by 60% to 1800 mg/l

II Anaerobic Lagoon

Ten days retention = 600 m^3.

If 4·5 m deep (i.e. 0·5 m freeboard) this will require a lagoon 12 m wide x 20 m long with 45° sloped sides. Anaerobic treatment can be expected to reduce the BOD and suspended solids as follows :-

BOD 4080 mg/l reduced by 50% to 2040 mg/l

Suspended solids reduced to about 1,000 mg/l

III Oxidation Ditch

Owing to the stronger nature of vegetable tanning wastes, it will be advisable to provide for five days retention in this scheme. This requires a working capacity of 300 m^3. If the channel dimensions are 1 m deep with 4 m top and 2 m bottom with [illegible] sides then the total length needs to be 100 m. This requires two long parallel trapezoidal channels, separated by a 2 m wide island, connected at each end by 5 m maximum radius semi-circular trapezoidal channels.

(a) Check on sludge loading

Using 6000 mg/l MLSS

Total daily BOD load to ditch = 60 m^3 x 2·5 kg/m^2 = 150 kg BOD/day.

Total mass of MLSS in ditch = 300 m^3 x 6 g/l = 1800 kg

$$\text{Therefore } L = \frac{150}{1800} = 0{\cdot}083 \text{ kg BOD/kg MLSS/d}$$

Since the BOD contributed by the vegetable tannins is likely to be rapidly oxidized the L of 0·083 is probably quite satisfactory (cf 0·05 for chrome tan effluent).

(b) Disposal of Final Effluent

The ditch should be operated in a manner similar to that suggested for chrome effluents and the schedule of final effluent decantation also will apply.

Exactly similar means of aeration will be required and, although the ditch is smaller the BOD load is similar and therefore the installed rotor oxygenation capacity must be identical to that for the chrome effluent.

viz: Four five foot rotors consuming 32 kwh/day.

IV Grass Plots

If effluent from the ditch is irrigated over 10 h each day, i.e. 6 m^3/h at an applied rate of 321/m^2h we require a grass plot area of 200 m^2. Therefore a plot 20 m x 10 m should suffice.

See overleaf Figs VII and VIII for diagrammatic outlines of treatment suggested.

FIG. VII

DIAGRAMMATIC OUTLINE OF TREATMENT SUGGESTED

CASE IX A - RURAL

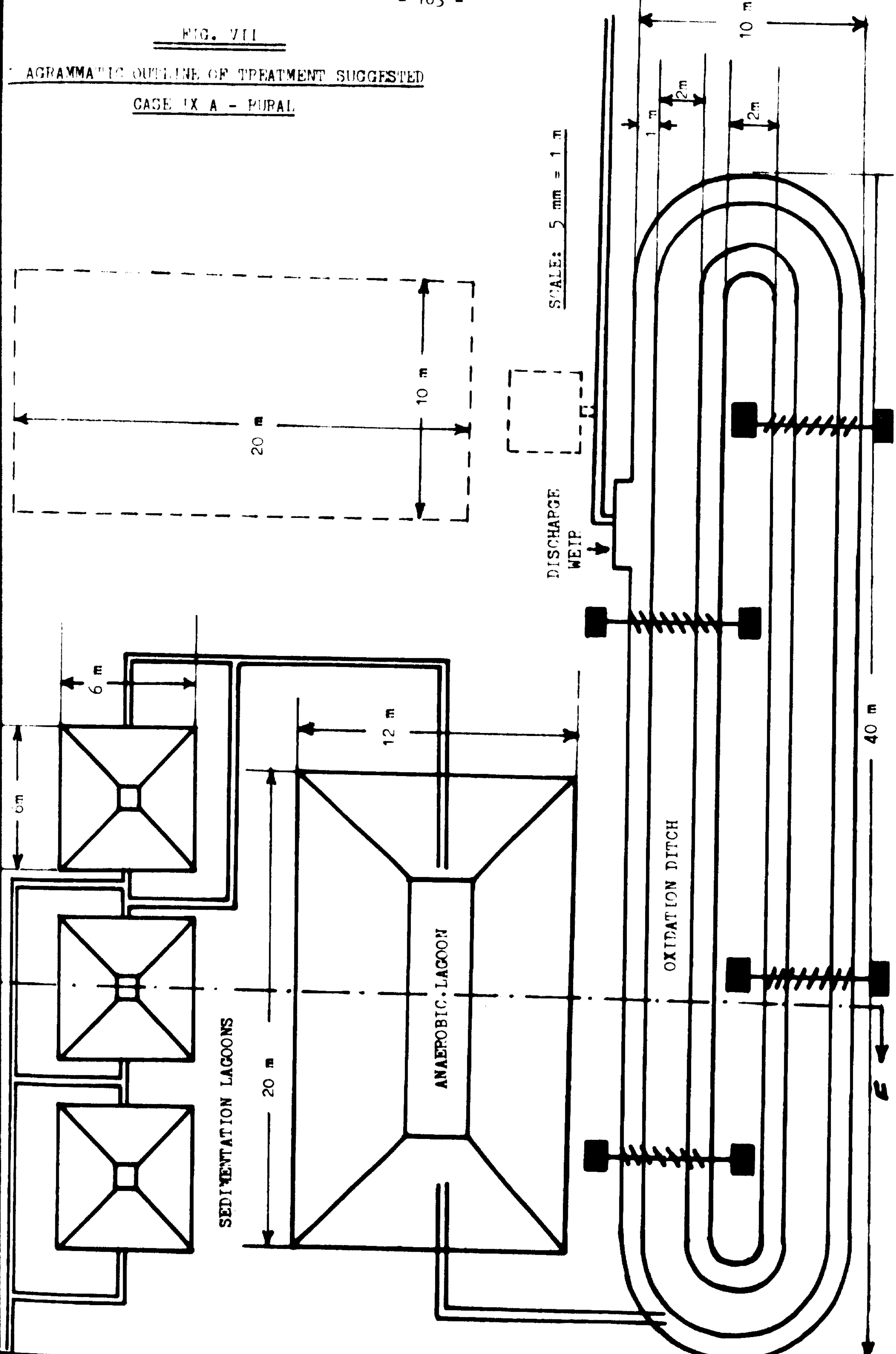
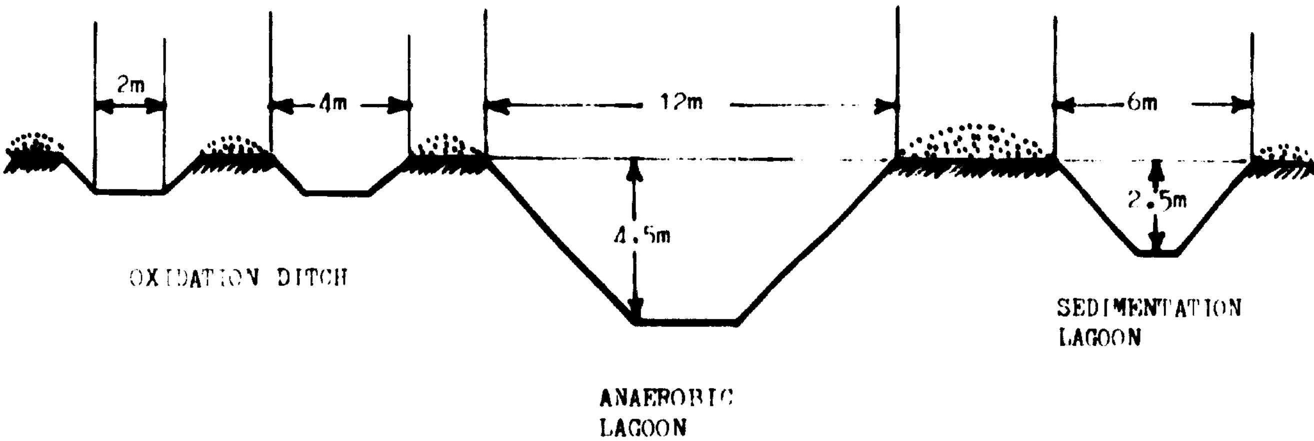


FIG. VIII

SECTION THROUGH TREATMENT PLANT RELATING TO

CASE IX A



SECTION THROUGH F - - - - - - F

SCALE: 5 mm = 1 m

B. Vegetable Tannery Effluent - Scheme for Urban Areas - Full Flow Balancing

In view of the strength of these liquors, and the case made out earlier for full flow balancing, only a scheme incorporating full flow balancing is considered economically practicable for urban treatment of vegetable tannery effluent.

I Mixing and Flow Balancing

Tank to hold one whole days flow - 60 m^3.

Suggested dimensions: 5 m x 4 m x 3 m deep

Pumped forward at a rate of 2·5 m^3/h.

II Sedimentation

(a) Vertical flow tanks

Allowing for upflow rate of 0·5 m/h a tank area of 5 m^2 is required. One tank only is needed. Suggested dimensions: 2·5 m x 2·5 x 2 m effective depth plus appropriate 60° sloped sludge hopper (as figs. in Annex XIV).

(b) Horizontal flow tank

With 6 h. retention at 2·5 m^3/h flow rate, capacity of single tank = 15 m^3.

If effective depth is 2 m then area must be circa 8 m^2.

Suggested dimensions are:

2 m wide x 4 m long x 2·5 m deep at inlet end sloped to 2·0 m deep at the outlet end. A spare tank will be needed for desludging.

Primary treatment should reduce BOD and suspended solids as follows :

BOD 5100 mg l reduced by 20% to 4080 mg l

Suspended solids 4500 mg/l reduced by 60% to 1800 mg/l

III High Rate Biological Filtration

Daily load of BOD = 60 m^3 x 4·08 kg/m^3 = 245 kg BOD/day

Applied at a load rate of 2 kg m^3 day the requirement will be 123 m^3 of filter medium. At a maximum depth of 3 m the filter area needs to be 41 m^2.

The high rate filter needs to be 7 m x 6 m x 3 m deep.

Construction and operation as previously discussed.

In view of the very low hydraulic loading rate on this filter it will be necessary to recirculate a relatively large volume of filter effluent - up to 10 to 1 so that a recirculation/feed pump rated at 25 m^3/h will be required.

Humus solids may be removed in a tank of similar design to that used for primary treatment but in view of the volume of recirculated effluent it will need to be larger in size. Recommended size would be 3·5 x 2·5 x 2 m effective depth, with appropriate 60° sloped sludge hopper.

IV Activated Sludge Treatment

The high rate treatment may be expected to reduce the BOD by 70% i.e. from 4080 mg/l to 1220 mg/l. The total BOD load remaining to be dealt with by the activated sludge stage will be 60 m^3 x 1·22 kg/m^3 = 73 kg BOD/day. At a safe sludge loading of 0·15 kg BOD/kg MLSS/day the system will require 490 kg MLSS. Using a MLSS concentration in the aeration tank of 3000 mg/l, an aeration tank capacity of 163 m^3 is required.

If the tank is 3 m deep, the area must be 54 m^2 and a tank 8·0 x 8·0 m x 3 m deep would thus suffice and provide some freeboard.

The vertical flow tank used to separate the activated sludge from the final effluent can be exactly similar in size and design to that used for primary treatment, but it must be a vertical flow tank to permit continuous sludge return. Sludge should be returned to the aeration tank at a rate equivalent to the flow of effluent i.e. 2·5 m^3/h.

V Rapid Gravity Filter

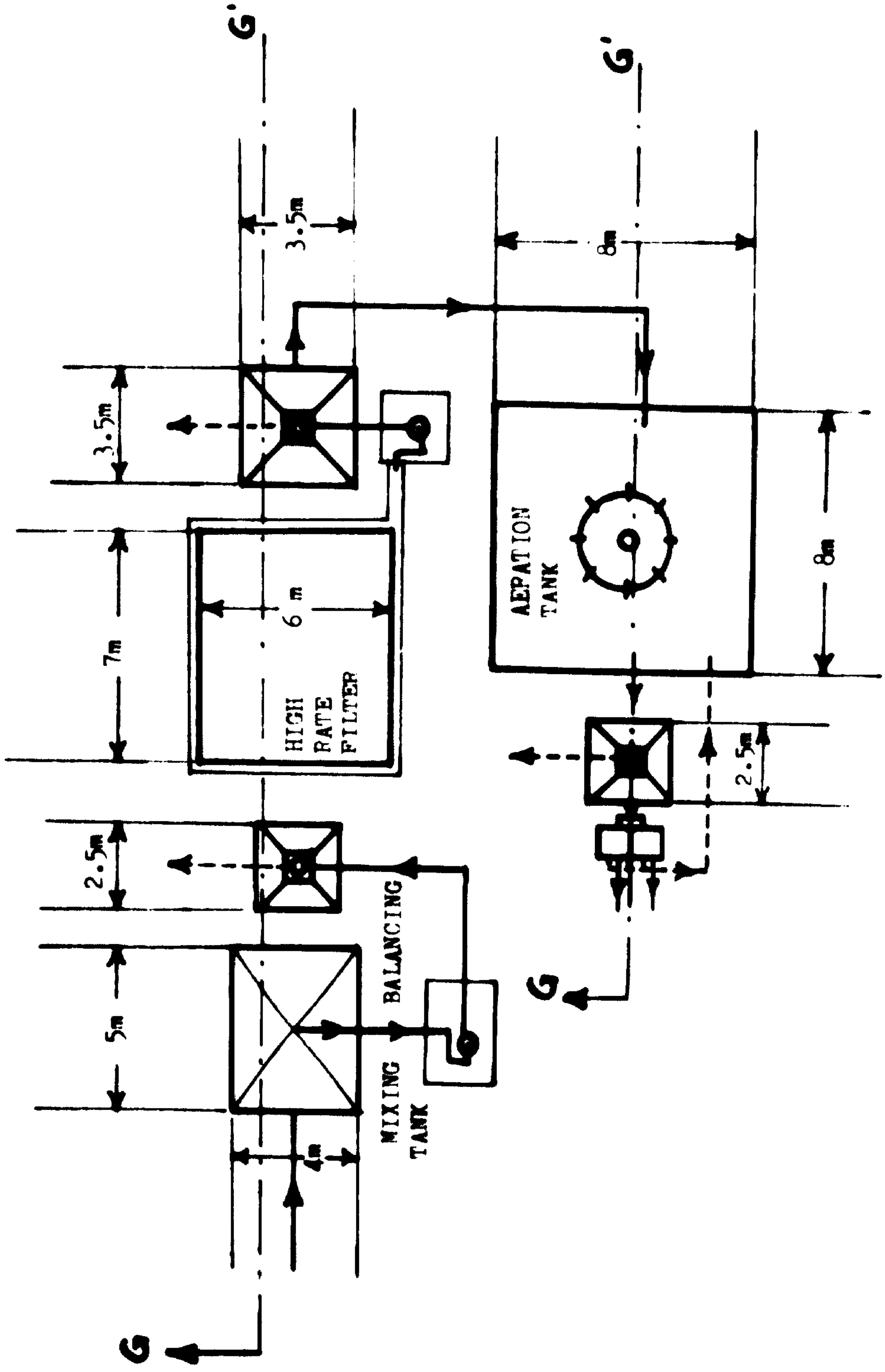
To treat a flow of 2·5 m^3/h at a design rate of 5 m^3/m^2 will require a filter area of 0·5 m^2. Clearly 1 m^2 will be more convenient to construct along the lines described previously.

See overleaf Figs. IX and X for diagrammatic outline of treatment suggested.

FIG. IX

DIAGRAMMATIC OUTLINE OF TREATMENT SUGGESTED

CASE IX B - URBAN - FULL FLOW BALANCING

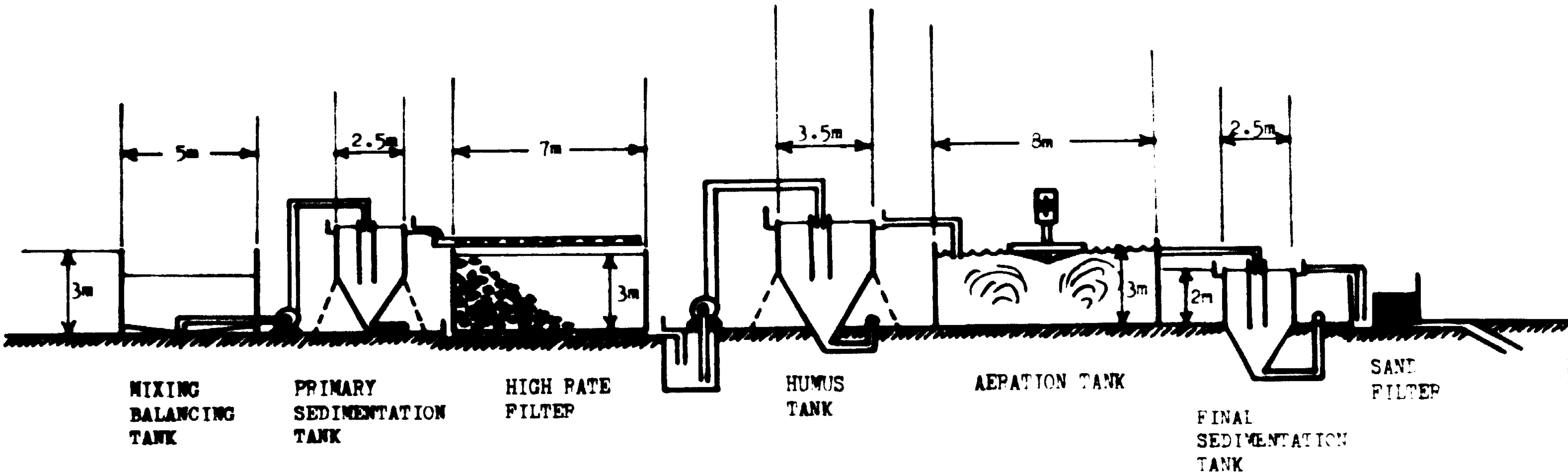


SCALE: 5 mm = 1 m

FIG. X

SECTION THROUGH TREATMENT PLANT RELATING TO

CASE IX B



SECTION THROUGH G - - - - - - G

SCALE: 5 mm = 1 m

C. Vegetable Tannery Effluent - Sludge

I. Sludge Production (from complete treatment)

(Applicable to Schemes IX A and B - See also Chapter X A)

- From suspended solids :

  60 m^3/d at 4500 mg/l or 4·5 kg/m^3 = 270 kg of dry solids/day

- From BOD removal :

  (Assuming that 35% of BOD is attributable to suspended solids).

  BOD after primary sedimentation = 4080 mg/l

  65% of 4080 = 2650 mg/l

  Therefore sludge production = 2·65 x 0·8 x 60

  = 127 kg/day of dry sludge solids

  Total = 270 x 127 = 397 kg/day

  (say 400 kg/d)

(NOTE: The higher BOD but appreciably lower suspended solids of the vegetable tanning effluent results in the biological secondary sludges forming a much greater proportion of the total sludge produced. This may mean that a greater degree of chemical conditioning will be required prior to mechanical dewatering but how much is impossible to predict.)

If the sludge is thickened to 5% solids content there will be 8 m^3 of wet sludge/day. (Treatment after high rate filter or anaerobic lagoon will produce 6·9 m^3/d. Primary treatment alone would result in about 4·3 m^3/d).

II Area of Drying Beds Required

8 m^3/day of wet sludge placed on beds to a depth of 0·5 m requires a bed area of 16 m^2.

Suggested bed size: 8 m x 8 m

Owing to the higher proportion of biological sludge, and because the primary sludge from vegetable tanning is generally more difficult to dry than that from a chrome process, at least four weeks should be allowed for drying. If a five day working week is in operation, 20 such beds will be required, covering an area 16 m x 80 m.

III Size of Filter Press required

(NOTE: As stated previously, owing to reasons given above, chemical conditioning of this sludge will undoubtedly be necessary prior to filter pressing.)

Making similar assumptions as in Chrome Tannery Sludges 8 m^3/d of sludge containing 5% of dry solids, i.e. 400 kg, but pressed into cakes containing only 30% of dry matter, the volume of the press cake would be about 1·5 m^3.

It should be possible to form press cakes 5 cm thick in a 1 m^2 filter press chemical conditioning, and an 8 hour pressing cycle. Hence 20 chambers will produce 1 m^3 of press cake. Therefore the filter press requirement is :

One 30 chamber filter press (5 cm chambers).

CHAPTER X

MISCELLANEOUS TREATMENT TECHNIQUES

A. Sludge Production and Disposal

Effluent treatment essentially is a solids/liquid separation process, the solids being removed from each stage of the treatment in the form of a thin slurry. The sludge from primary sedimentation generally contains from 5 to [illegible]% of dry matter, whilst settled humus sludge from biological filters or surplus activated sludge contain from 1 to 2% of dry matter, and are capable of thickening on standing to 3 or [illegible]% of dry matter.

The backwash waters from sand filters contain only [illegible] of dry matter and usually these are recirculated to an earlier stage of treatment.

Traditionally sludge has been disposed of to land, either directly as a slurry or else after drying on drainage beds to a solids content of 20 to 30%. If the beds are properly constructed the latter method can be quite effective given reasonably good weather, but a relatively large area of land is required. In many countries the increased cost of labour and escalating land values have necessitated a resort to mechanical methods of dewatering sludge, such as filter presses, vacuum filters and centrifuges for new works.

However, many older established municipal works in Europe still utilize drying beds to dry digested sludge, and in some instances, the digested slurry is disposed of directly onto agricultural land.

Anaerobic digestion of the sludge is generally considered essential (but still not always practised) prior to land disposal, in order to kill pathogenic bacteria and parasites such as tape-worm cysts. In all probability, digestion will not be necessary in the case of tannery sludges, but where disposal to agricultural land is contemplated, it will be advisable to seek advice, especially where the land is used for cultivating crops for human consumption. (See also Volume I of this Report).

In rural areas land disposal will undoubtedly be the most economic solution and whether this is by direct disposal as a slurry or after drying on beds will depend on local conditions and the needs of farmers.

If drying beds are used these should be constructed as shown in the Annexes. They essentially consist of an area of perforated drainage tiles (especially made) covered with coarse clinker or gravel topped by a layer of 1 mm graded sand. As some sand is removed with each batch of dried sludge, periodic replenishment is necessary.

The drying beds should be constructed in units of sufficient capacity to accept one days production of sludge, poured on to a depth of [illegible] m, which should then be left to drain and dry. It is most undesirable to "double-stack" by placing one batch of sludge on top of another.

In urban areas disposal by tankering out of town will almost certainly be the most economic solution. However, in cases where this is not possible, mechanical dewatering will have to be used. Filter presses have been well proved in service, and although vacuum filters are used these require more skilled supervision, whilst centrifuges are still relatively unproven (but rapidly gaining ground).

For the purposes of this report filter presses have been selected as the simplest alternative where mechanical sludge dewatering is unavoidable, and calculations have been made to indicate very roughly the size of equipment which would be needed so that cost can be obtained in individual cases.

Generally the quantities of sludge produced by the rural and urban schemes discussed earlier will be of the same order. It is true that the extended biological processes of the rural schemes will produce less sludge per unit mass of BOD removed (0·4 kg/kg as compared with 0·8 to 1·0 for the urban scheme), and also some sludge will be destroyed in the anaerobic lagoon. However, these factors cannot be precisely quantified and in the interest of simplicity no allowance for them has been made.

The actual calculated examples for plant requirements relate to <u>full treatment</u> and smaller quantities of sludge might be expected from partial treatment. However, in the case of those particular process liquors which contain very high concentrations of suspended solids, most of the sludge will be produced by the primary sedimentation stage. Although to err on the side of caution in calculations presented, only 60% has been assumed to be removed, it is quite likely that removal of 80% of the suspended solids will be achieved in the first stage and this must be allowed for in sludge calculations. As is seen later, biological sludge represents a relatively small proportion of the total sludge produced.

B. The effect on Treatment Requirements of Operating a Hair-saving Process

It has been demonstrated by van Meer [100] and others that the pulping liquors from a hair-destroying depilation process contribute up to one third of the total BOD and COD content of tannery wastes.

Although many authorities conclude that the extra mechanization and skill needed in handling, associated with hair saving processes would be disadvantageous in the context of this exercise, it must be pointed out that the implementation of such a process could permit a significant reduction in the size of those treatment units, which are based mainly on BOD load, viz. the high rate filter, the activated sludge treatment stage of the urban schemes and the oxidation ditch of the rural schemes.

Since the design criteria relating to anaerobic lagoons appears to be somewhat vague, the effect of reduced BOD loads on the size of this unit has been ignored in the present report.

An alternative to using a hair saving process per se might be to segregate the unhairing liquors and to treat these separately to remove dissolved proteins (by acidification and coagulation followed by settlement)[illegible] before mixing them with the other waste liquors. It is thought however that the pH must be depressed well below the iso-electric point of the proteins before reasonably full precipitation is achieved, i.e. to about pH 2·[illegible]. Hence, the quantity of acid required to achieve this will be financially quite significant. Moreover, since the remaining waste liquors are predominantly below pH 7·0 the addition of more alkali (e.g. lime) will be necessary to adjust the pH of the final mixed wastes to a level suitable for either biological treatment or even for discharge to a foul sewer.

It must also be stressed that it will be most essential to remove the sulphide content of the waste unhairing liquors prior to acidification in order to avoid the release of extremely toxic hydrogen sulphide gas. Whilst this may in any case be necessary where only partial treatment prior to discharge to a foul sewer is envisaged, for example in urban schemes, it may not always be the case, in which event it would have to be regarded as an additional cost. (The method of sulphide removal is discussed later).

The following provides a rough indication of the reductions in plant capacity which may be made possible by eliminating hair pulping liquors from the mixed wastes.

I Chrome Leather Tannery Effluent

(a) Rural Scheme (Ref Chapter VIII A)

The circuit length of the oxidation ditch could be reduced by 56 m. This would be effected by reducing the overall length of the "doubled-up" ditch by 28 m. It would also be possible to dispense with one of the four aeration rotors.

(b) Urban Scheme (Limes balancing only) (Ref. Chapter VIII B)

The high rate filter could be reduced in size to 13·[illegible] m x 13·7 m by 3 m deep. The activated sludge aeration tank capacity could be reduced to [illegible] m^3. This could then conveniently be contained in three aeration tanks measuring [illegible] m x [illegible] m x 3 m deep, and saving <u>one</u> aeration rotor.

(c) Urban Scheme (full flow balancing (Ref Chapter VIII C)

The high rate filter could be reduced in size to [illegible] m x [illegible] m x 3 m deep. The activated sludge aeration tank capacity could be reduced to 3[illegible] m^3. This could then conveniently be contained in two aeration tanks measuring 7·[illegible] m x 7·[illegible] m x 3 m deep.

II Vegetable Sole Leather Tannery Effluent

(a) Rural Scheme (Ref. Chapter IX A)

The circuit length of the oxidation ditch could be reduced by 3[illegible] m. This would be effected by reducing the overall length of the "doubled-up" ditch by 1[illegible] m. It would also be possible to dispense with <u>one</u> of the four aeration rotors.

(b) Urban Scheme (Ref. Chapter IX B)

The high rate filter could be reduced in size to 5·[illegible] m x 5·2 m x 3 m deep. The activated sludge aeration tank capacity could be reduced to [illegible] m^3. This could then conveniently be contained in a tank measuring [illegible] m x [illegible] m x 3 m deep.

[illegible] The Effect on Treatment Requirements of Processing Only to the "Wet Blue" Stage

In order to simplify the treatment schemes presented here, it has been assumed that processing leather only to the "wet blue" stage would reduce the volume of effluent by about [illegible]%. Since most of the waste liquors produced subsequent to chrome tanning are relatively low in organic matter there would be little effect on the total <u>mass</u> of BOD discharged, but the reduced dilution would result in a stronger mixed effluent. Consequently processing to the "wet blue" stage would only influence the size of those treatment units which are designed entirely on hydraulic flow, i.e. sedimentation tanks.

In the case of rural schemes, the lagoons already have a less than theoretical capacity owing to their sloped sides, and it is suggested that they could be reduced in size (if processing to wet blue stage) <u>only</u> if a significant saving in costs is indicated in the particular circumstances. It would <u>not</u> be desirable to reduce the number of lagoons.

In the case of the urban schemes the vertical flow tanks could theoretically be reduced in area by 25%, which would also reduce the depth of the pyramidal base. However, the [illegible] m deep operating depth should not be reduced.

It must be emphasized, however, that the settling characteristics of the, even more concentrated, wastes will not necessarily be similar, and in the absence of precise information on the settlement of such strong wastes it is suggested that for safety the 25% reduction should not in fact be implemented.

D) The Removal of Sulphide from Waste Unhairing Liquors.

The chief difficulty associated with the sulphide content of tannery wastes arises when they are discharged to sewerage systems, and become diluted with less alkaline sewage, which may result in the evolution of hydrogen sulphide gas. Hydrogen sulphide is extremely toxic at quite low concentrations and would constitute a serious hazard to sewer workers (See Vol I Chapter III). In addition atmospheric sulphide, as well as that in solution, can through various mechanisms cause serious deterioration to the fabric of sewers (102)

Experience has indicated that the level of sulphide in tannery effluents is unlikely to cause serious difficulties in their subsequent biological treatment. However the reduced volumes of water which are proposed in the foregoing sections of this report, and the consequent reduced dilution of the sulphide wastes, will result in appreciably higher concentrations of sulphide in the mixed effluents. It may therefore become necessary to reduce the sulphide concentration to achieve optimum performance of the intensive biological processes used in the urban schemes. However, the considerable dilution afforded by the oxidation ditch system makes it seem unlikely that such pretreatment would be necessary for the rural scheme, unless an odour problem is likely to arise.

Sulphide liquors are most satisfactorily treated before mixing and dilution with other waste liquors, as a smaller oxidation tank can be used. It is important therefore to make provision in the tannery for the segregation of all the sulphide bearing liquors.

A simple process for the treatment of sulphide wastes by catalysed oxidation was developed at the British Leather Manufacturers Research Association [101]. The process consists in aerating the sulphide liquors in the presence of small amounts of added manganous sulphate.

The precise dimensions of the treatment tank depend on the method used to aerate the liquors, which may be by diffused air or by mechanical surface aeration, but the tank capacity should be sufficient to contain one day's production of waste lime-sulphide liquors and their associated sulphide bearing wash waters.

In diffused air plants the tank should be tall in relation to its depth in order to use the air efficiently, but the depth should not exceed 6 m which would otherwise necessitate using expensive air compressors instead of Rootes type blowers.

The time required for treatment depends on the initial concentration of sulphide, the intensity of aeration and the concentration of catalyst. As a working rule of thumb, it has been found that an aeration intensity of 0·3 m^3/minute per square metre of tank cross sectional area and a catalyst concentration of 50 to 100 mg/l of Mn^{++} has proved satisfactory in reducing the concentration of sulphide from 2000 mg/l to about 20 mg/l in 4-6 hours. The recommended intensity of aeration can be achieved by placing standard activated sludge dome diffusers at 30 cm centres on the base of the tank. It must be emphasized that only fine bubbles produced by specially made air diffusers will provide satisfactory results.

An alternative to the use of diffused aeration is to use mechanical surface aerators which also were originally developed for use in activated sludge systems. These operate by agitating the surface of the liquor and achieve aeration by splashing and the entrainment of fine air bubbles.

In these systems however the depth of liquor in the tank should preferably not exceed 2·5 m and the tank must be made sufficiently large in area to contain the appropriate volume of liquor.

E. Separate Treatment of Vegetable Tan Liquors.

Vegetable tan liquors exert exceptionally high biological and chemical oxygen demands (BOD and COD) and, depending on the degree of uptake (exhaustion) achieved during the tanning process the "spent" liquors may contribute very substantially to the BOD and COD of the final mixed wastes. BOD values as high as 20,000 mg/l have been encountered for such liquors and, moreover, the ratio of COD to BOD may be as high as 5 or 7 to 1, very different to that found with more conventional wastes such as domestic sewage, for which the ratio is 3 to 1. This could be interpreted as indicative of a less easily biodegradable waste and, certainly, vegetable tanning wastes can still exert a relatively high residual COD even after fairly complete biological treatment has removed the bulk of the BOD [103]. As well as possessing a high residual COD the treated liquor though clear is markedly coloured. Indeed some of the organic compounds appear to have been darkened by their partial oxidation.

Normally an appreciable amount of the organic materials present in spent vegetable tan liquors are precipitated on admixture with the other waste liquors containing calcium ions and proteinaceous matter. In the plant designs recommended earlier, ample opportunity for this co-precipitation to occur is afforded by the provision of suitably sized mixing and balancing tanks (or in settling lagoons) and it is certainly debatable whether this could be improved upon by separate treatment with added chemicals. One advantage of separate chemical treatment might be to reduce the colour and residual COD of final effluents by achieving more effective precipitation.

The design and size of suitable separate treatment plant will clearly depend on individual circumstances, but the "tan exhaustion" or concentration of residual tannins in the spent liquor will be a most important factor. For the foregoing reasons it is not possible to quote hard design data. If such treatment were envisaged it would be necessary, therefore, to conduct laboratory and pilot scale tests to develop and evaluate a suitable process. The objective of such tests would be to achieve satisfactory reductions in COD and colour. It would also be essential to obtain a suitably rapid settlement of the precipitated solids and their compaction into a readily filterable sludge. Very promising reductions in COD and colour in laboratory bench scale experiments have been reported using combinations of lime, copperas (ferrous sulphate) and alum (aluminium sulphate).

Owing to the intermittent production of the vegetable tan wastes it is suggested that treatment would be simplified if a batch system were used. Chemicals could then be dosed sequentially to a gently stirred tank which could be subsequently used for settlement and, finally, decantation of the clarified liquor.

Whichever method is finally selected, the cost of chemicals should be estimated and, in particular, a careful note should be made of the quantity and filterability of sludge produced. If caution is not exercised it is possible to produce a situation in which 80% or more of the sludge solids originate from the coagulant chemicals used in treatment!

To sum up it may be said that chemical treatment of the separated spent vegetable tan liquors might reduce the size of subsequent biological treatment plant, and may also reduce the colour and residual COD of the final effluent. However, the possibly substantial cost of chemicals used, and the extra treatment plant, must be weighed against any potential savings in biological plant or, where a partially treated liquor is to be discharged, in trade effluent charges.

F. Mechanical Equipment and Suppliers

1 Surface Aerators

In the treatment schemes outlined earlier there are three different processes in which it is necessary to cause atmospheric oxygen artificially to be dissolved in the liquor being treated. These are the oxidation ditches of the rural schemes, the activated sludge units of the urban schemes and the sulphide oxidation plants.

The dissolution of atmospheric oxygen may be brought about by either diffused aeration, in which compressed air is passed through the liquid via porous ceramic fine-bubble air diffusers set on the base of the tank, or by mechanical surface aerators which dissolve oxygen by surface agitation and splashing, and by the entrainment in the liquor of fine bubbles of air.

In the oxidation ditch system it is most convenient to use horizontally rotating steel brush aerators which essentially are rotating cylinders with many protruding steel spines which revolve at great speed with the tips (100 - 150 mm) of the spines dipping into the water. The advantage of this mechanism is that it also serves to impel the liquor around the ditch.

For the urban activated sludge units it is also recommened that surface aeration be used owing to its relative simplicity and ease of maintenance. In this case aerators which rotate around a vertical axis were selected. This type of device has now found preference for use in sulphide aeration plants because of easier maintenance, also because it seems that improved dispersion of the manganous catalyst is achieved.

It would be possible for reasonably adept engineers/fitters to fabricate any of these devices, but a number of them are protected by patents and this situation would need to be assessed from a national point of view.

G. Effluent Standards from Each Stage of Treatment

I. It is important to emphasize that, owing to the appreciably lower quantity of water employed in the recommended tanning process, i.e. 15 l/kg of hide processed, the waste liquors requiring treatment will be more concentrated than those resulting from a more conventional tanning process which generally uses 40 - 60 l of water per kilogram of salted hide processed. Since there is very little experience of the treatment of these more concentrated tannery wastes, in which incidentally toxic or inhibitory substances may be present in higher (i.e. less diluted) concentrations, the prediction of the likely standard of effluent quality which will be achieved by the various treatment stages must be subject to a certain degree of speculation. It is however recognised that some guidance is desirable in the present study and an attempt to provide this is given in the accompanying tables.

For the purpose of calculating the required capacities of subsequent treatment units the reduction in the concentration of BOD and suspended solids achieved by the primary sedimentation stages were assumed to be pessimistically low in order to err on the side of safety. In practice much greater reductions in BOD and suspended solids may be achieved by the primary stages, and the tables therefore include a range of values for BOD and suspended solids in the primary settled effluents.

However, the efficiency of the anaerobic lagoons which was assumed to be [illegible] - [illegible]0% removal of BOD (based on Sastry's observations of [illegible]% reduction in BOD ([illegible])) may be overoptimistic, and in fact [illegible]0% reduction may be more generally achieved in practice, and this possibility is reflected in the range of values quoted. It may be pointed out however, that this should be adequately compensated for by the effective primary stage, and the generously sized oxidation ditch.

It should also be remembered that <u>temperature</u> has an appreciable effect on biological treatment processes, and, within the operative range of the micro-organisms involved, a 10 degree centigrade increase in temperature will double the rate of metabolic activity. The various treatment units have been sized assuming a "normal" temperature range <u>in the effluent</u> (not atmospheric) of not less than 10°C and not greater than [illegible]0°C.

The anticipated effluent standards for each treatment scheme may be seen in Table I.

II. Method of Final Disposal

It was recommended in the earlier discussion that primary treatment by mixing and settlement should be the minimum treatment received by any effluent. This would produce an effluent of Category A standard which would be suitable only for discharge to a foul sewer for subsequent treatment at a communal sewage works.

TABLE 1

EFFLUENT STANDARDS

Stage of Treatment *(i)	BOD (mg/l)	Suspended Solids (mg/l)	Effluent Category
Chrome-side Upper Leather Tannery - Rural Scheme			
Raw Mixed Effluents	3,600	10,000	-
After Primary Sedimentation	2,100-2,700	1,000-4,000	A
Effluent from anaerobic lagoon	600-1,000	500-1,000	B
Effluent from Oxidation Ditch	20-40	30-60	C
Glass Plot Effluent	10-20	5-15	D
Chrome-side Upper Leather Tannery - Urban Scheme			
Raw Mixed Effluents	3,600	10,000	-
After Primary Sedimentation	2,100-1,700	1,000-4,000	A
Effluent from High Rate Filter	800	400	B
Effluent after Activated Sludge Treatment	20-50	30-60	C
Sand Filter Effluent	10-20	5-15	D
Vegetable Sole Leather Tannery - Rural Scheme			
Raw Mixed Effluents	5,100	4,500	-
After Primary Sedimentation	2,500-4,100	1,000-1,800	A
Effluent from Anaerobic lagoon	1,500-2,500	500-1,000	B
Effluent from Oxidation ditch	20-40	30-60	C
Glass Plot Effluent	10-20	5-15	D
Vegetable Sole Leather Tannery - Urban Scheme			
Raw Mixed Effluents	5,100	4,500	-
After Primary Sedimentation	2,500-4,100	1,000-1,800	A
Effluent from High Rate Filter	1,200	400	B
Effluent After Activated Sludge Treatment	20-50	30-80	C
Sand Filter Effluent	10-20	5-15	D

*(i) See Volume I, Chapt. V for possible costs for each treatment stage

The effluents from the primary biological stages of Category B standard, would be suitable for discharge to estuarine or tidal waters affording considerable dilution (after taking into account the ebb and flow of the tide and the tidal "hold-up" in estuarine waters).

It may also be acceptable to discharge a category B effluent to a non-tidal river where the dilution with clean water is greater than 500 times, but this would also depend on the subsequent use of the river.

Effluent of category C standard should be suitable for discharge to most rivers and streams as well as lake waters. Discharge to underground aquifers via boreholes may also be considered, but the opinion of the local water supply authority should be sought in the latter case.

Only in cases where the discharged effluent receives a very low dilution by river water or where the river forms a source of raw water used for potable supply should it be necessary to produce an effluent of such high quality as in category D.

ANNEX I - A

COMPOSITION OF TYPICAL "NON-ENVIRONMENTALLY SOUND" TANNERY EFFLUENT

		Chrome Tannage		Vegetable Tannage
ph			ca. 10	
Total solids	mg/l		10,000	
Total ash	mg/l		6,000	
Suspended solids	mg l	2,500		1,500
Ash in suspended solids	mg l	1,000		500
Settled solids (2 h)	ml/l	100		50
BOD_5	mg/l	900		1,700
$KMnO_4$ - value	mg O_2/l	1,000		2,500
COD ($K_2Cr_2O_7$)	mg/l	2,500		3,000
Sulphide	mg/l		160	
Total nitrogen	mg/l		120	
Ammonia nitrogen	mg/l		70	
Chrome (Cr)	mg/l	70		-
Chloride (Cl^-)	mg/l		2,500	
Sulphate ($SO_4^{=}$)	mg/l		700	
Phosphor (P)	mg/l		1	
Ether Extractable	mg/l		350	

ANNEX I - B

AMOUNTS OF POLLUTION PER TON OF RAW MATERIAL (SALT WEIGHT)

		Chrome Tannage		Vegetable Tannage	Range
Alkalinity	eq/t		750		
Total solids	kg/t		675		350 - 1,250
Total ash	kg/t		375		250 - 450
Suspended solids	kg/t	150		75	70 - 200
Ash in suspended solids	kg/t	60		25	25 - 60
Settled solids (2 h)	m^3/t	6		3	1·5 - 7·5
BOD_5	kg/t	60		85	40 - 100
IOD	kg/t		10		
$KMnO_4$ - value	kg O_2/t	70		120	
COD ($K_2Cr_2O_7$)	kg/t		175		120 - 280
Sulphide	kg/t		7		
Total Nitrogen	kg/t		10		
Ammonia nitrogen	kg/t		3		
Chrome	kg/t	4·5		0	
Chloride	kg/t		160		
Sulphate	kg/t		40		
Phosphor	kg/t		0·07		

ANNEX II

Use of Water by the use of continuous rinsing (cycle A) vs. batch washing (cycle B)

(After (4) (5),)

	Cycle A (100 l/kg salt weight)					Cycle B (25 l/kg salt weight)				
	Volume of effluent l/kg	% of total tannery	Float l/kg	Rinsing l/kg	Float as % of total vol.	Vol. of effluent l/kg	% of total tannery	Float l/kg	Washing l/kg	Float as % of total vol.
Soak	24	24	6	18	25	9	36	6	3	67
Unhairing	37	37	1,6	35,4	4,2	7,8	31	1,8	6	23
Delime to tan	11	11	2	9	18	4	16	2	2	50
Aftertreatment	28	28	1,5	26,5	5,5	4,5	17	1,4	3	31
Total fabrication	100		11,1	89	11	25		11,2	14	45

ANNEX III

Amounts of pollution from the unhairing (per kg salt weight)

(pre-flashed cow hides, relatively short-haired)

Dosage os water and chemicals	Total solids g	Fixed solids g	BOD_5 g	Organic N g	Ammonia-N g	Alkalinity eq	Sulphide g
A. 300% H_2O, 5% lime (75%), 1,6% S^{--}	103	71	22	5,2	0,1	0,69	5
B. 200% H_2O, 3,2% lime (75%), 1,1% S^{--}	80	43	22	5,3	0,1	0,26	3,3
C. 200% H_2O, 2% lime (75%), 0,85% S^{--} 1)	[illegible]	30	22	5,3	0,1	0,2	2,5
D. as C, but with re-use of the supernatant and precipitation of protein from the sediment 2) (Added for use: 55% H_2O, 1,5% lime (75%), 0,75% S^{--}) 1).	30	15	9	2	0,05	0	0
E. Enzyme unhairing with alkaline treatment	90	60	13	3,2	0,2	0,15	0,07

1) Estimated values.

2) Including surplus amount of pollution in effluent from subsequent washing and processes which follow from the re-use.

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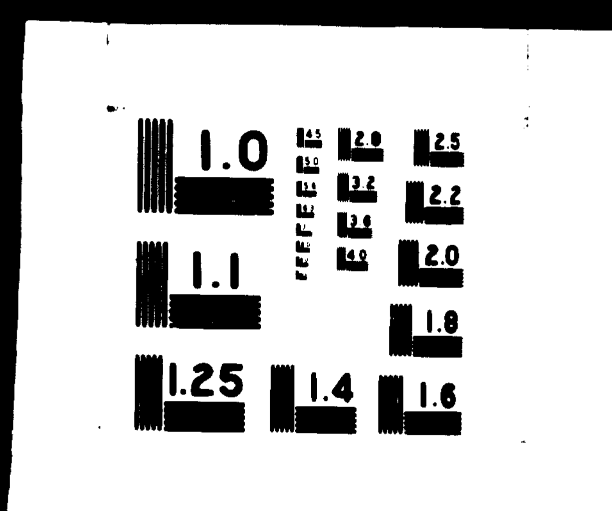


ANNEX IV

Chrome balance, side leather production.

	Chrome offered Cr_2O_3 % on pelt weight	% of amount offered					Amounts of chrome g/kg salt weight		
		Good tanning liquor	Drain and wring liquor	Washing	Neutralization and re-tan	Leather*	Offered	In leather*	In effluents
Typical practice	2,5	25	5	3	2	65	20,5	13,3	7,2
High chrome fixation	1,95	13	1,7	1,1	0,3	84	16,0	13,4	2,6

*Grain Leather, split and shavings

ANNEX V

Water consumption for wet processing (practicable technologies).

	Drums	Hide processors	Keller-Heidemann apparatus
	% on salt weight		
Soaking	2x250	50+100	2x200
Unhairing	200	100	150
Washing	2x300	2x75	3x200
	% on pelt weight		
Deliming-bating	10	10	60
Washing	200	2x50	200
Pickling-chrome tanning	40	40	40
	l/kg salt weight		
Total consumption to Cr tanning inclusive	15,3	5,6	14,4
	% on shaved weight		
Wet after-treatments, grain leather	850	600	-
	l/kg salt weight		
Total consumption for wet processing (both grain leather and split)	19,6	8,4	-

ANNEX VI

(CONVENTIONAL PROCESS)

Typical material balance for vegetable tanning.

	Given		Discharged with effluent % on salt weight				
	Pure tan % on pelt weight	Total solids % on salt weight (A)	Dissolved organic solids	Dissolved inorganic solids	Suspended solids	Total solids (B)	B in % of A
1. Sole leather	37	56	18	0,6	1,6	20	37
2. " "	33	48	12	0,6	1,4	14	29
3. Technical leather	26	38	12	0,5	1,1	14	36
4. Upholstery leather	28	30	5,8	0,3	0,8	6,9	23

Hide protein in the effluent not included.

The solids are discharged both directly from the tanning and with the effluent from washing, bleaching and sammying. (For example 2, the amount of dissolved solids discharged directly is about 10% on the salt weight.)

ANNEX VII

Amounts of pollution, chemicals saving drum technology. Production of chrome leather from salted hides.

Processes	Water l/kg salt weight	Tot. sol.	Fixed sol.	Vol. sol.	BOD_5	COD	Org. N	Amm. N	S^{--}	Cr
		g/kg salt weight								
Raw hide preservation	0.3	90	75	15	3.9	7.4	1.25			
Soaking	5	150	135	15	12	25	1.5			
Unhairing and washing	7.2	87	42	45	26	65	6.4	0.1	2.7	
Deliming-bating and washing	2.6	28	8	20	3	7	0.9	1.3	0.1	
Pickle-chrome tanning	0.5	131	93	38	5	13	0.75			2.4
Wet aftertreatment	4.3	30	6	24	4	13				
Pasting, finishing	1.6	1	0	1	0.6	1.3				
Sanitary, cleaning	2.2	2	1	1	0.7	1.5	0.02			
From raw water	—	6	5	1	0.1	0.4				
Total (preservation not included)	23.4	435	290	145	51	126	9.6	1.4	2.8	2.4
Normal practice	60	590	420	170	60	160	12 (Org. N + Amm. N)		8	5.5
Theoretical minima *)		250	160	90						
Total, wet blue production (excl. preservation)	15.3	400	281	119	48	110	9.6	1.4	2.8	2.2

*) for processing of salted hides

ANNEX VIII

Amounts of pollution, chemicals saving drum technology. Production of vegetable sole leather from salted hides.

Processes	Water l/kg salt weight	Tot. sol.	Fixed sol.	Vol. sol.	BOD_5	COD	Org. N	Amm. N	S^{--}
		g/kg salt weight							
Raw hide preservation	0.3	90	75	15	3.9	7.4	1.25		
Soaking	5	150	135	15	12	25	1.5		
Unhairing and washing	7.2	84	38	46	26	65	6.4	0.1	2.5
Deliming and washing	2.6	18	8	10	0.2	0.5	0.05	0.9	0.1
Pickle	—	34	24	10	4	11	0.7		
Tanning and bleaching	2.0	135	15	120	25	75			
Sanitary, cleaning	1,8	2	1	1	0.6	1.3	0.02		
From raw water	—	4.3	3.6	0.7	0.1	0.2			
Total (preservation not included)	18.6	427	225	202	68	188	8.7	1.0	2.6
Normal practice	48	500	250	250	70	190	11		7
Theoretical minima*)		250	160	90					

*) for processing of salted hides

ANNEX IX

Amounts of pollution. Chrome leather production. Drum technology.

		Water 1/kg salt weight	Total solids	Fixed solids	Volatile solids	BOD_5	COD	Organic bound nitrogen
			g/kg salt weight					
Salted hides	Tannery	23.4	435	290	145	51	126	9.6
	Preservation	0.3	90	75	15	4	7	1.3
	Tannery+pre-servation	23.7	525	365	160	55	133	10.9
Salted, pre-fleshed hides	Tannery	20.9	413	271	142	50	124	9.5
	Preservation	0.3	80	67	13	4	7	1.1
	Tannery+pre-servation	21,2	493	338	155	54	131	10.6
Green, pre-fleshed hides		20.9	301	146	155	53	129	10.4
Dried hides		23.5	328	160	168	56	134	11.1

All figures are calculated on the basis of the weight of salted, not fleshed hide.

ANNEX I

Amounts of pollution. Chrome leather production. Drum technology.

		Water l/kg salt weight	Total solids	Fixed solids	Volatile solids	BOD_5	COD	Organic bound nitrogen	Ammonia nitrogen	Sulphide	Chrome
			g/kg salt weight								
Salted hides	Unhairing as in Annex VII	23,4	435	290	145	51	126	9,6	1,4	2,8	2,4
	Enzyme unhairing	23,4	430	300	130	37	89	6,4	1,1	0,07	2,4
	Re-use of unhairing liquor and protein precipitn.	22,0	400	275	125	38	91	6,3	1,4	0	2,4
	Re-use of chrome liquor	23,0	388	250	138	50	125	9,6	1,4	2,8	0,54
	Re-use of unhairing and chrome liquor	21,6	353	235	118	38	90	6,3	1,4	0	0,54
	Re-use of less polluted liquors 1)	14,8	431	287	144	51	126	9,6	1,4	2,8	2,4
	Re-use of u.l., c.l. and l.p.l.	16,9	351	233	118	38	90	6,3	1,4	0	0,54
Salted hides	Re-use of u.l. c.l. and l.p.l. (preservation included)	16,9	441	308	133	42	97	7,6	1,4	0	0,54
Green, pre-fleshed hides	Re-use of u.l., c.l. and l.p.l.	16,9	218	90	128	40	93	7,1	1,4	0	0,54

All figures are calculated on the basis of the weight of salted, not fleshed hide.

1) liquors from 2. wash after unhairing, wash after deliming and washings from the after-treatments (or part of this)

ANNEX XI

Amounts of pollution. Vegetable sole leather production. Drum technology.

		Water l/kg salt weight	Total solids	Fixed solids	Volatile solids	BOD_5	COD	Organic bound nitrogen	Ammonia nitrogen	Sulphide
			g/kg salt weight							
Salted hides	Processing as in Annex VIII	18,6	427	225	202	68	188	8,7	1,0	2,6
	- do. -, incl. preservation	18,9	517	300	217	72	195	10,0	1,0	2,6
	Enzyme unhairing	18,6	430	235	195	57	158	6,3	1,1	0,07
	Re-use of unhairing liquor and protein precipitation	17,2	392	210	182	55	153	5,4	1,0	0
	Re-use of less polluted liquor 1)	13,5	425	223	202	68	188	8,7	1,0	2,6
	Re-use of u.l. and l.p.l.	14,8	391	209	182	55	153	5,4	1,0	0
	- do. -, incl. preservation	15,1	481	284	197	59	160	6,7	1,0	0
Green, pre-fleshed hides	No re-use	15,9	293	81	212	70	191	9,5	1,0	2,6
	Re-use of u.l. and l.p.l.	12,2	257	65	192	57	156	6,2	1,0	0

1) liquors from 2. wash after unhairing and from wash after deliming.

All figures are calculated on the basis of the weight of salted, not fleshed hide.

ANNEX XII

Amounts of pollution. Hide processor technology.

			Water l/kg salt weight	Total solids	Fixed solids	Volatile solids	Sulphide
				g/kg salt weight			
Chrome leather	Salted hides	No re-use	12,2	428	284	145	2,7
" "	" "	Full re-use	9,7	348	230	118	0
" "	**Green,pre-fleshed** hides	Full re-use	9,7	215	87	128	0
Vegetable leather	Salted hides	No re-use	9,0	421	220	201	2,5
" "	" "	Full re-use	6,7	388	206	182	0
" "	**Green,pre-fleshed** hides	Full re-use	6,7	255	63	192	0

All figures are calculated on **the basis of the weight of salted, not fleshed hides.**

ANNEX XIII

MODIFIED "BAILEY" PROCESS

Process	No Re-use	With Re-use = Saving
Soak and Wash		
1 st Wash	300% s	
2 nd Wash	200% s	350%
Lime	100% s	100%
1 st Wash	150% s	
2 nd Wash	150%	
Delime and Bate	100% s	
Wash	100%	
Pickle and Chrome Tanning	60% s	
Wash	100% s	
Neutralization	100%	
Wash	100%	
Retanning	50% s	
Wash	50%	
Fat-liquoring and Dyeing	50% s	
1 st Wash	50% s	
2 nd Wash	50% s	
	1710%	450%

1710% (17 l/kg)

Saving - 450%

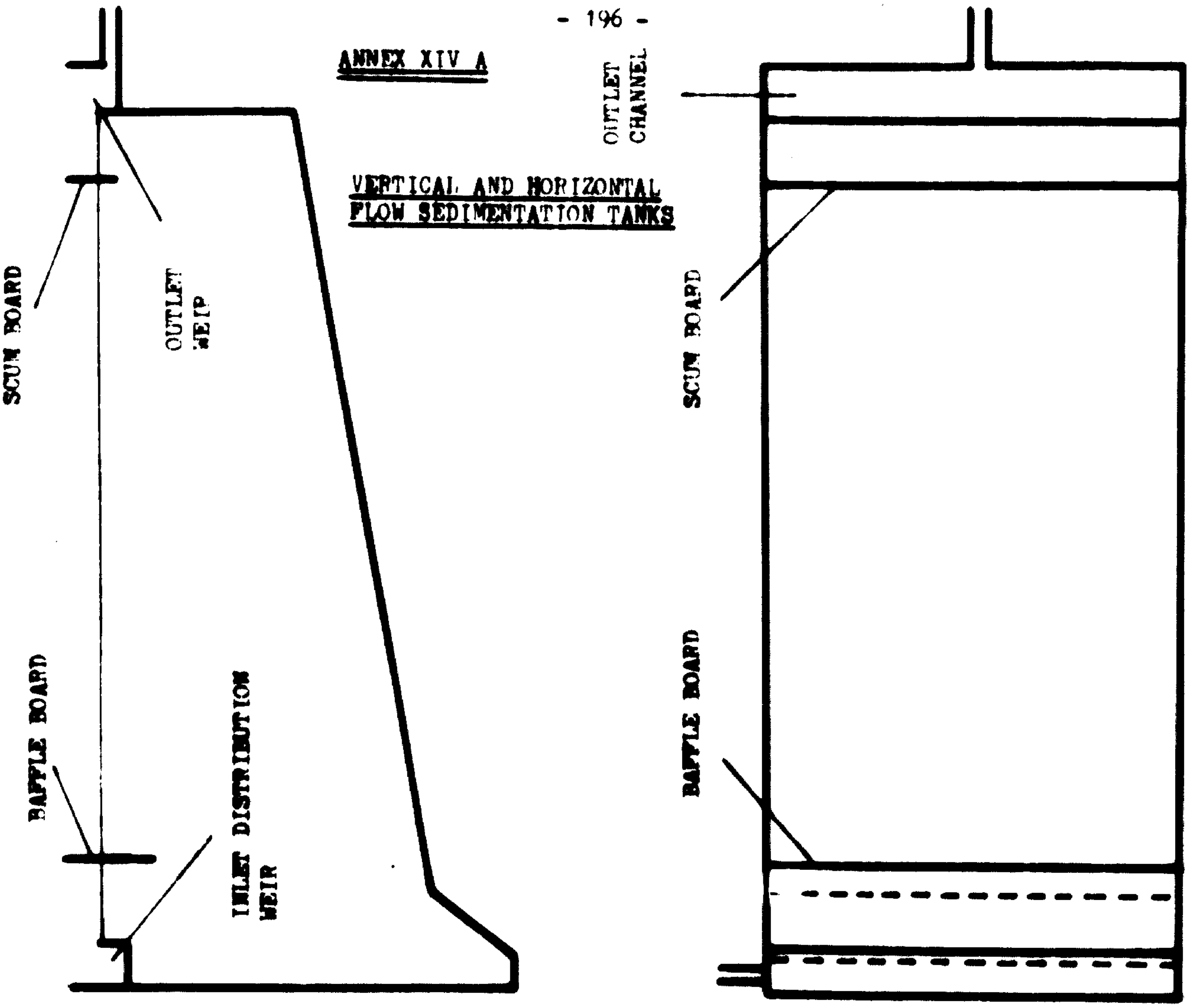
Water Usage 1260%

or about 13 l/kg

s = direct to factory effluent collection system

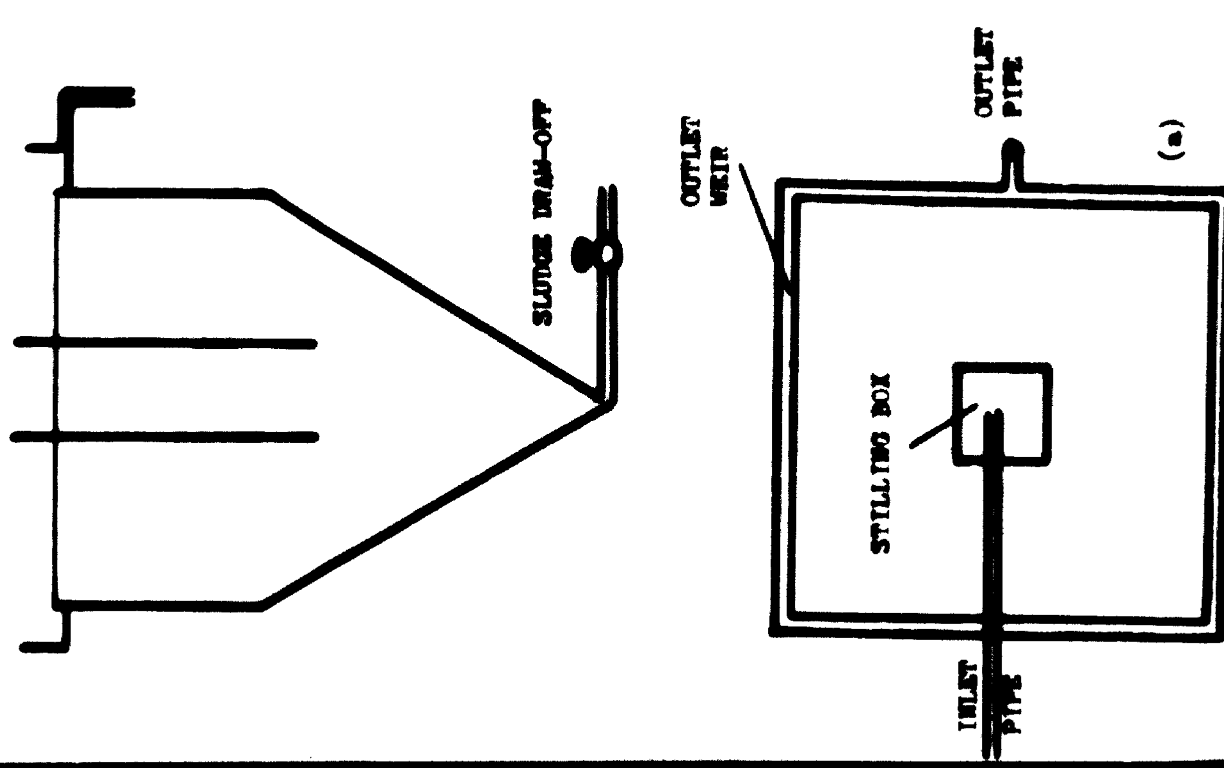
ANNEX XIV A

VERTICAL AND HORIZONTAL FLOW SEDIMENTATION TANKS



(b)

HORIZONTAL FLOW SEDIMENTATION TANK



(a)

VERTICAL FLOW SEDIMENTATION TANK

ANNEX XIV B

MECHANICALLY SCRAPED RADIAL FLOW SEDIMENTATION TANKS

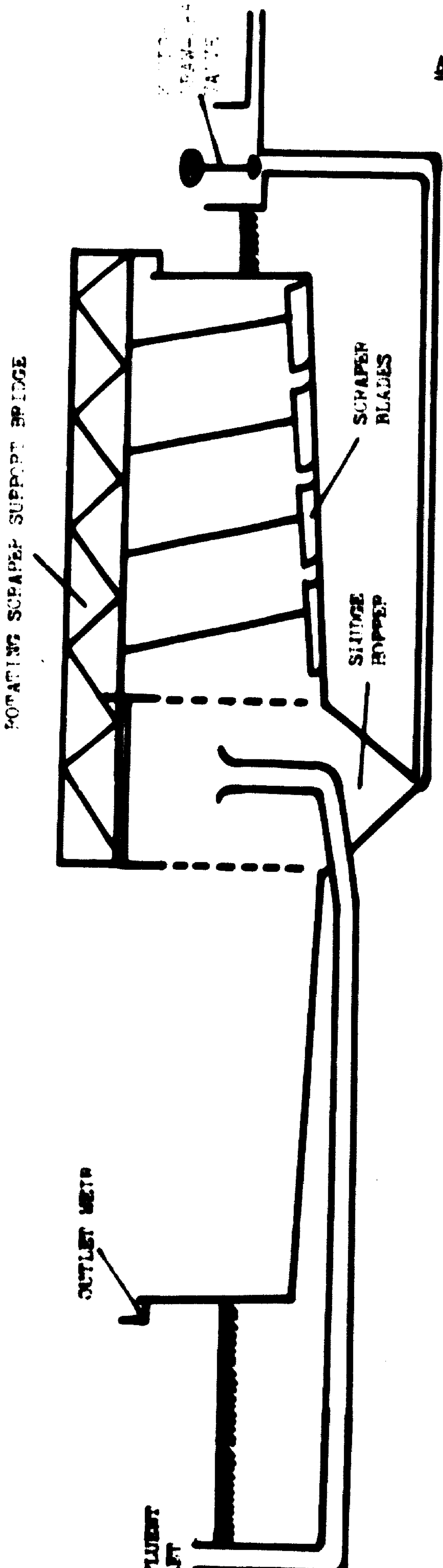


FIG. 1 (c)

ANNEX XV

GLOSSARY RELATING TO TERMS USED IN VOLUME II PART II

BOD	Biochemical oxygen demand exerted in 5 days
COD	Chemical oxygen demand
Activated Sludge	The mass culture of bacteria and other micro-organisms which bring about the purification of effluents by the breakdown and metabolism of organic matter.
MLSS	"Mixed liquor suspended solids" - the concentration of activated sludge solids in the aeration tank.
Sludge loading	The daily mass of BOD fed to unit mass of MLSS, i.e. $\frac{\text{kg of BOD/day}}{\text{kg of MLSS in plant.}}$
High rate filter	A biological filter (i.e. percolating or trickling filter) which is similar in all respects to a conventional filter except that it is loaded at a rate ranging from 1 to 8 kg of BOD/m^3 of filter medium per day as compared with a loading of about 0·1 kg BOD/m^3d for a conventional filter. Although a lower standard of effluent is obtained the filter removes a much greater total mass of BOD per unit volume of medium.
Filter BOD loading	The daily mass of BOD applied to unit volume of the filter medium, i.e. kg BOD/m^3d.
Filter hydraulic loading	The daily volume of effluent applied to unit volume of the filter medium, i.e. m^3 of liquor/m^3d.

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