



EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)

**Reference Document on Best Available Techniques
for the Tanning of Hides and Skins**

February 2003

EXECUTIVE SUMMARY

This reference document on best available techniques in the tannery industry reflects an information exchange carried out according to Article 16(2) of Council Directive 96/61/EC. The document has to be seen in the light of the preface, which describes the objectives of the document and its use.

Scope

The scope of the BREF for the tanning industry is based on Section 6.3 of Annex I of the IPPC Directive 96/61/EC as 'Plants for tanning hides and skins where the treatment capacity exceeds 12 tonnes of finished products per day'. The types of hides and skins are restricted to those of ovine and bovine origin, because the production capacities for any other type of raw material for the production of leather and furs are far below the threshold value in the Directive.

Structure of the industry (Chapter 1)

The tannery operation consists of converting the raw hide or skin, a highly putrescible material, into leather, a stable material, which can be used in the manufacture of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Amongst these, tanning is the fundamental stage, which gives leather its stability and essential character. The production of raw hides and skins depends on animal population and slaughter rate and is related mainly to meat consumption.

On the world scale, significant cattle populations are to be found in the US, Argentina, the former USSR and the EU. Sheepskins originate predominantly in New Zealand, Australia, the Near East and the EU. For both bovine hides and sheepskins, the EU is a net importer, indicating the necessity of proper storage and means of transport for the typically salted raw materials.

The EU is the world's largest supplier of leather in the international marketplace. Italy is the major country in Europe in terms of establishments, employment, production and turnover. It accounts for 15 % of the world's cattle and calf leather production and 65 % of EC production. Spain ranks second and – with France, Germany and UK – accounts for most of the balance in the European leather industry. The EU's share of world markets is tending to shrink with the development of the leather industry in other regions of the world such as Asia and the Americas.

Tanneries in Europe are SMEs; only 10 of them are reckoned to employ more than 200 people. Only 1 % employ between 101 and 200 people and 8.5 % employ between 21 and 100 people. Companies are generally family businesses with a long tradition. The most important outlet for EU tanneries' production is footwear, with a share of 50 %. The clothing industry takes approximately 20 % of all finished leather produced in the EU. Leather for furniture and automotive upholstery represents some 17 % and the leather goods sector 13 % of EU tanners' output.

Leather tanning is a raw materials and labour intensive industry. Raw materials account for 50 to 70 % of production costs, labour 7 to 15 %, chemicals about 10 %, energy 3 %. EU tanners' environmental costs are estimated at about 5 % of their turnover.

The tanning industry is a potentially pollution-intensive industry. The environmental effects that have to be taken into account comprise not merely the load and concentration of the classic pollutants, but also the use of certain chemicals: e.g., biocides, surfactants and organic solvents. Tanneries in Europe usually discharge their waste water effluents to large waste water treatment plants, which are either municipal treatment plants or plants operated for large tanning

complexes. Few tanneries discharge directly to surface water. Most tanneries discharging to sewer have some form of on-site effluent treatment installed, ranging from pre-treatment to biological treatment. Of world tanneries, 80 – 90 % use chromium (III) salts in their tanning processes. The degree of toxicity of chrome is perhaps one of the most debated issues between the tanning industry and authorities.

Applied processes and techniques (Chapter 2)

The production processes in a tannery can be split into four main categories: hide and skin storage and beamhouse operations, tanyard operations, post-tanning operations and finishing operations. After the hides and skins are flayed from the carcass at the abattoirs, they are delivered to the hide and skin market, directly to the tannery or to the fellmongery. Where necessary, hides and skins are cured before transport to the tannery in order to prevent the hides and skins from putrefying. Upon delivery to the site, hides and skins can be sorted, trimmed, cured and stored pending operations in the beamhouse.

The following processes are typically carried out in the beamhouse of a tannery (see the glossary): soaking, unhairing, liming, fleshing and splitting. Typically, the following processes are carried out in the tanyard: delimiting, bating, pickling, and tanning. Sheepskin tanneries may degrease the skins prior to, or after, pickling or after tanning. The tanned hides and skins are tradable intermediate products (wet-blue) as they have been converted to a non-putrescible material called leather. Processes typically carried out in post-tanning operations are: samming, setting, splitting, shaving, retanning, dyeing, fatliquoring and drying. At this stage the leather is called 'crust'. Crust is also a tradable intermediate product. Finishing operations include several mechanical treatments as well as the application of a surface coat. The selection of finishing processes depends on the specifications of the final product. Tanneries generally use a combination of the following processes: conditioning, staking, buffing, applying a finish, milling, plating and embossing.

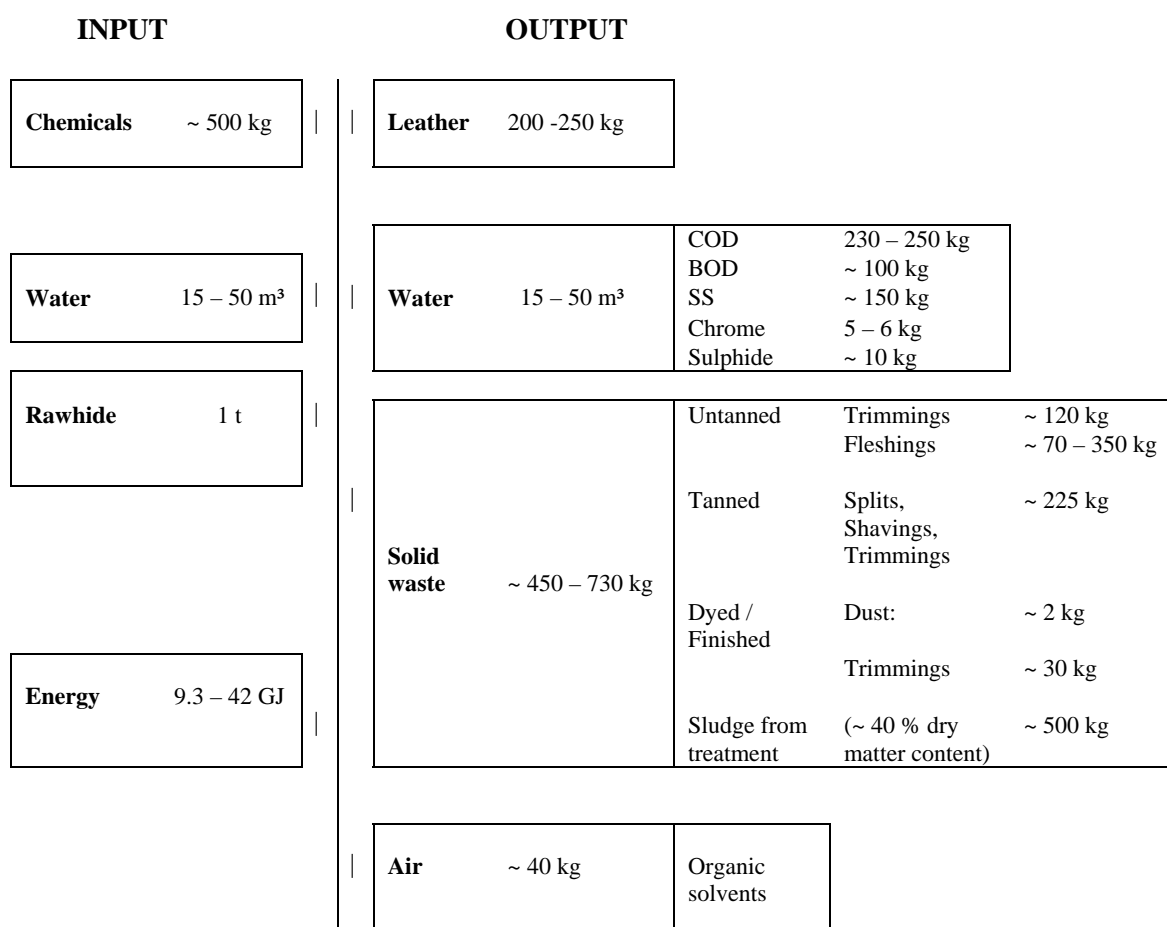
Current emission and consumption levels (Chapter 3)

Due to the wide versatility of tanneries, both in terms of the types of hides and skins used and the range of products manufactured, the reported emission and consumption levels are generally indicative. They serve to indicate the ranges of emission and consumption levels that can be seen in a wide range of tanneries. Where possible, a range for consumption and emission levels for particular processes is given. The figures strongly depend on the raw material processed, the quality and specifications of the final product, the processes chosen and local requirements.

The environmental impacts of tanneries originate from liquid, solid and gaseous waste streams and from the consumption of raw materials such as raw hides, energy, chemicals and water.

The main releases to waste water originate from wet processing in the beamhouse, the tanyard, and the post-tanning operations. The main releases to air are due to the dry-finishing processes, although gaseous emissions may also arise in all other parts of the tannery. The main sources of solid wastes originate from fleshing, splitting and shaving. A further potential source of solid waste is the sludge from the effluent treatment plant (but this is not an on-site activity in all tanneries). However, many of these wastes may be classified as by-products as they may be sold as raw materials to other industry sectors.

The following figure gives an input / output overview for a conventional (chrome-tanning) process for bovine salted hides per tonne of raw hide treated.



The following table shows the consumption level of the main process chemicals, tannage agents and auxiliary chemicals for a conventional tanning process for salted, bovine hides.

Chemical consumption	%
Standard inorganic (without salt from curing, acids, bases, sulphides, ammonium-containing chemicals)	40
Standard organic, not mentioned below (acids, bases, salts)	7
Tanning chemicals (chrome, vegetable and alternative tanning agents)	23
Dyeing agents and auxiliaries	4
Fatliquoring agents	8
Finish chemicals (pigments, special effect chemicals, binders and cross-linking agents)	10
Organic solvents	5
Surfactants	1
Biocides	0.2
Enzyme	1
Others (sequestering agents, wetting agents, complexing agents)	?
Total	100

The most environmentally significant and most used tanning agents (with their auxiliaries) are:

Type of tannage	Tanning agents used	Auxiliaries used
Chrome tannage	Basic sulphate complex of trivalent chrome	Salt, basifying agents (magnesium oxide, sodium carbonate, or sodium bicarbonate), fungicides, masking agents (e.g. formic acid, sodium diphthalate, oxalic acid, sodium sulphite), fatliquors, syntans, resins
Other mineral tannages	Aluminium, zirconium, and titanium salts	Masking agents, basifying agents, fatliquors, salts, syntans, resins etc.
Vegetable tannage	Polyphenolic compounds leached from vegetable material (e.g. quebracho, mimosa, oak)	Pre-tanning agents, bleaching and sequestering agents, fatliquors, formic acid, syntans, resins etc.

Techniques to consider in the determination of BAT (Chapter 4)

Efficient raw material and energy usage, optimum process chemical utilisation, recovering and recycling of waste and substitution of harmful substances are important principles of the IPPC Directive. For tanneries the focal points are water consumption, efficient use and substitution of potentially harmful process agents and waste reduction within the process in conjunction with the recycling and re-use options.

Substitution of substances

Biocides may be used in the curing, soaking, pickling, tanning and post-tanning processes. Halogenated organic compounds have been used for a long time in tanneries and halogenated biocides are still sold. Sodium- or Potassium-di-methyl-di-thiocarbamate is considered to be a less environmentally significant bactericide, due to its lower persistency and toxicity levels.

Halogenated organic compounds can be substituted in almost every case, but there are exceptions. One of the exceptions addressed is the dry-degreasing of Merino sheepskins. The degreasing is carried out in closed machines with abatement for air and waste water releases; the solvent is automatically distilled and re-used. Other exceptions addressed are HOC-containing fatliquors and water-repellent agents used for waterproof leathers.

In order to reduce VOC emissions in the finishing process, water-based systems are increasingly favoured over systems based on organic solvents. Another option to reduce VOC emissions is the use of low-organic solvent finishing systems. Base coats are generally water-based. If very high topcoat standards of wet-rubbing, wet-flexing and perspiration are required, then solvent-based systems cannot always be substituted by water-based systems. In some situations, upholstery leathers for automotive and furniture use are examples of such applications. In order to achieve equal characteristics with low-organic solvent and water-based systems, cross-linking agents for the finishing polymers often have to be used. Binders based on polymeric emulsions with low monomer content are used in finishings to replace the conventional polymeric products. The use of cadmium and lead in pigments is not common in European tanneries; it should be stressed, however, that any use should be discouraged.

Surfactants are used in many different processes throughout the tannery, e.g., soaking, liming, degreasing, tanning and dyeing. The most commonly used surfactant is NPE, because of its emulsifying property. The main alternatives in the leather industry are alcohol ethoxylates but, when very fatty sheepskins have to be degreased – to date – only NPE can achieve the desired result.

Complexing agents such as EDTA and NTA are brought into the water as sequestering agents. Because of their biodegradability, EDSS and MGDA are possible substitutes, but no information has been submitted about the use of those substances in the tanning process.

Ammonium deliming agents can be wholly or partially substituted by carbon dioxide deliming. The technique is easy to handle and can be automated. It requires the installation of a pressurised storage tank for CO₂, diffusers and a warming chamber that has to be checked regularly by trained personnel. With the use of CO₂ deliming, a 20 – 30 % decrease in total Kjeldahl nitrogen emissions and a 30 – 50 % reduction in BOD in the effluent from the tanning process can be achieved. A complete substitution is possible for bovine hides, but the process can be very slow with thicker hides. In deliming ovine skins, the problem with the use of CO₂ is the amount of sulphide that is released and has to be abated. The payback time of the investment costs is estimated to be 1 - 2 years.

Ammonium deliming agents can also be substituted by weak organic acids, such as lactic acid, formic acid and acetic acids. The ammonia levels in the waste water are reduced, but these agents increase the COD load. The organic agents are about 5 - 7 times more expensive than ammonium salts. Because of the increase of the COD load and because organic agents are more expensive, the viability has to be analysed carefully for each specific case.

Concerning the dyeing process, achievable techniques and technologies to reduce the impact on the environment are:

- to substitute powder dyestuffs with liquid ones, to reduce dust emissions
- to select dyestuffs and auxiliaries with lower environmental impact, e.g. substitute poor-exhausting dyestuffs with high-exhausting ones, substitute dyestuffs containing high levels of salts with dyestuffs containing a limited amount of salts, etc
- to avoid the use of ammonia as penetrating agent, as ammonia can be substituted completely in most cases
- to substitute halogenic dyes by vinyl sulphone reactive dyes to reduce the AOX load.

The use of high-exhaustion fatliquor systems will result in lower COD levels. An exhaustion of fatliquor equivalent to 90 % of the original offer can be considered achievable. Applying solvent-free or low-solvent content mixtures will result in less solvent emissions. This also applies to water-repellent agents which are preferably also free of metal salts, although the substitution of metal salts (chrome, aluminium, zirconium, calcium) as fixing agents is not applicable for very high standards of water resistance.

There is already movement away from the use of brominated and antimony-containing fire retardants. This is due to their potentially toxic combustion products. The natural successors will almost certainly be phosphate-based.

Process-integrated measures

For curing and soaking the processing of fresh (unsalted) hides will result in a significant reduction of the level of salt in the effluent. An emission load of 5 kg/t chloride when salt-free hides are processed, compared with an emission load of 65 kg/t chloride from an average soaking process using salted hides, is reported. When the hides can be processed within 8 - 12 hours after slaughter, the hides do not need to be chilled. Chilled hides have to be processed within 5 - 8 days. When longer transport times are necessary, e.g. because the hides have to be transported overseas, the energy consumption can become prohibitive because of transporting extra weight (ice) or the use of refrigerated units. In those situations the only alternative is to use salt. Fresh hides may not always be available, e.g. where a significant proportion of hides are imported or exported. The decision whether to process cooled or salted hides also depends very much on the end-product. Where salt is used in conserving the hides, various options exist to achieve a reduction of the salt input. They are mainly a question of optimising the management of the process and the input of chemicals rather than applying particular techniques.

In the unhairing and liming process for bovine hides, the use of hair-save technologies can reduce the emission levels of several parameters. Reported reduction data are:

Parameter	Reduction in waste water from the liming/unhairing section
COD	- 60 %
TKN	- 35 %
Sulphide	- 50 %

Hair-save processes for bovine hides are well known but they demand precise operating conditions and control. The technique involves manipulating the conditions of alkalinity and reducing the agent in such a way that the hair comes out of the follicle without being pulped and without destroying the hair shaft. A recirculation system with a screen is used to separate the intact hair. The hair is usually landfilled or, where possible, used as new raw material (e.g. fertiliser) elsewhere. The technique requires high capital investment for existing tanneries and may not be viable where, on the one hand, landfill is the only disposal option for the saved hair and, on the other, the waste water treatment plant can handle the high organic load of burned hair and high sludge production is not a problem because the sludge is treated and therefore suitable for re-use as, e.g. fertiliser. A careful balance has to be struck, taking each case on its merits.

A total substitution of the sulphides used as an unhairing agent for bovine hides is currently not possible in practice, but the use of enzyme preparations can reduce the consumption of sulphides. It is reported that COD and sulphide are reduced by 40 – 70 % each. This technique is not suitable for sheepskins, because the upgrading of the wool as a saleable by-product hinders the reduction in the sulphide consumption. When processing sheepskins that are already dewoolled by painting, the recycling of the spent sulphide liquor is common practice.

In most cases, lime splitting is an environmentally better option than splitting after tanning (blue splitting). Lime splitting allows the grain layer and the flesh layer to take different routes – e.g. different tannages or different end uses – and the split may be used for the manufacture of gelatine or collagen casings for foodstuffs. Following lime splitting the consumption of all chemicals and water in the subsequent processes is reduced, because only the parts of the hides processed into leather are treated. The structure and chemical nature of the liming process for a lime splitting operation involves a higher degree of penetration and swelling of the hide fibres. This is not suitable for making firmer leathers, such as shoe upper leather. Limed pelts are more difficult to handle than either tanned or crust leathers and therefore lime splitting is less accurate than blue splitting and is not suitable if a more uniform and accurate thickness is needed in the final product.

Not enough information is available about sheepskin degreasing to enable a conclusion to be drawn on whether the substitution of solvent degreasing systems by aqueous degreasing systems will result in a better environmental performance. This is because it is difficult without further information to compare the environmental impact of the use of organic solvent with that of the use of surfactants.

Spent pickle liquors from the pickling process can be recycled into the pickling process or re-used in the tanning process in order to reduce the amount of salt and effluent discharged to sewer. Another technique to reduce the amount of salt and effluent is the use of a short pickle float. Some processes use an average pickling float of about 100 %; this can be reduced to 50 - 60 %, which means that the use of 0.5 - 0.6 m³ water per tonne fleshed pelt is achievable.

Although tanning can be performed with different tanning agents, about 90 % of leathers are tanned with chromium salts. Another well-known process is vegetable tanning. The vegetable tanning process is not seen as an alternative to the chrome tanning process, because first of all they are two completely different processes to produce different products. Another reason is that research has shown that selection of a certain tanning agent (chromium or a vegetable agent) will not in itself reduce the environmental consequences of the process. A comparison of chromium with other mineral tanning agents is not possible because the environmental impact of the latter tanning agents has not been assessed in enough detail. In chrome tanning, amongst others, the following techniques are discussed:

1. Increasing the efficiency of chrome-tanning. The conventional chrome tanning carried out in long floats is characterised by poor exhaustion; 30 – 50 % of the chrome applied being lost with the waste water. The chrome uptake can be increased up to 80 % through careful control of pH, float, temperature, time and drumspeed.
2. High-exhaustion chrome tanning methods. In this technique the tanning agents used are modified to enhance uptake up to 90 %. In conventional tanning (without chrome recovery) 2 - 5 kg/t raw bovine hides of chrome salts are released via the spent liquors; with high-exhaustion chrome tanning this quantity can be reduced to 0.05 - 0.1 kg/t raw bovine hides. Because of the low concentration, the remaining chrome in the effluent is not recovered.
3. For the conventional chrome tanning process, chrome recovery through precipitation and separation; as mentioned above, chromium from high-exhaustion chromium processes is not recovered. Chrome recovery is from the chemical point of view a simple process with excellent environmental results, but it needs careful analytical control and it requires special equipment. Chrome recovery is applied by individual tanneries (e.g. in Germany), whereas Portugal and Italy each have one common chrome-recycling unit, although the Italian one is available only for the tanneries situated in the Santa Croce tanning area. The recovered chrome sulphate can be recycled into the tanning process by replacing 20 – 35 % of the "fresh" added chrome tanning salt. Certain types of leathers (e.g. split) can be tanned with 100 % recovered chromium. Efficiencies of 95 to 99.9 % of chrome precipitation are reported; concentrations, measured as total chrome in a daily composite sample, after sedimentation or flotation of the separate chrome-containing effluent (before mixing) of 1 - 2 mg/l and even < 1 mg/l can be achieved. A survey in Italy of the economic costs has revealed that for a single medium-to-large tannery, the installation of a chrome recovery unit can cost about EUR 520000 (estimated value). Based on Greek conditions (year 1990 - 1991), the maximum payback period for installing a chrome recovery unit is 1.6 years. In India two different examples of running a chrome recovery unit show payback periods of 1 and about 1.6 years (reference years 1994 and 1995).

Vegetable tanning systems with a high degree of tanning exhaustion (~95 %) are available. Common systems are the counter-current (pit-system) and drum tanning with recycling of the tanning material. When (in combination with vegetable tanning) syntans and resins are used, products with low-phenol, low-formaldehyde and low acrylic acid monomer content are the best alternatives.

In the post-tanning operations of retanning, chrome fixation and neutralisation, careful control of processing parameters such as the levels of chemical inputs, the reaction time, the pH and the temperatures can enhance the exhaustion of the post-tanning treatment agents. Chrome fixation of the tanning agents can be improved by allowing the necessary ageing time for the tanned leather prior to the post-tanning processes. An optimum input of the neutralising salts ensure that the pH of the liquor and the leathers by the end of the process are close, ensuring either no or low unused salt discharged to waste water.

Forced drying of leather is among the most energy intensive processes in the tannery. Natural air-drying does not consume energy but is not applicable under all circumstances, as it requires time and favourable climate conditions. Considerable reductions in energy consumption can be achieved by optimising the mechanical dewatering processes prior to drying.

Applying a surface coat on the leather is an important source of VOC emissions. The use of roller coating, curtain coating, HVLP spray guns and air-less spray guns result in less VOC emissions compared to conventional operations (with an efficiency as low as 30 %). HVLP, or airless spraying raises the efficiency to 75 %. But conventional spraying techniques have to be applied to achieve very thin finishes on, e.g. aniline and aniline-type leather. Suitable abatement techniques for VOC emissions are wet scrubbing, absorption, bio-filters, cryogenic removal or incineration.

Water management and treatment

For bovine hides it is reported that a water consumption of 40 - 50 m³/t raw hide can be cut to 12 - 30 m³/t, if the tannery operates efficient technical control and good housekeeping. For the processing of calf skins, about 40 m³/t and sometimes more is needed. There are several techniques or technologies to improve the efficiency of water use. The first step involves optimisation of water consumption and lowering the consumption of chemicals used in the process and in the waste water treatment. It is found that in tanneries with poor water management only 50 % of the water consumed is actually used in the process. Running water washes is one of the major sources of water wastage. In those cases it is important to improve the matching of water flow to the requirements of the process and to use 'batch' versus 'running water' washes. The use of short-float techniques can be achieved either by modifying the equipment to utilise short floats, or by installing modern tannery machines. With a combination of batch washing and short floats, savings of water consumption up to 70 % can be achieved, compared with a conventional process. The re-use of waste water can decrease water consumption considerably, but tanners are reluctant to re-use it because of the risk that residual chemicals or other contents in the water will damage the hides.

In order to carry out effluent treatment in the most effective manner, flow segregation is useful to allow preliminary treatment of concentrated waste water streams, in particular for sulphide- and chrome-containing liquors. And although a reduction of water consumption does not reduce the load of many pollutants, concentrated effluents are often easier and more efficient to treat. Where segregation of flows is not possible, thorough mixing of chrome-bearing effluents and other effluent streams improves the efficiency of the effluent treatment plant because the chromium tends to precipitate out with the protein during pretreatment. The treatment of chrome-containing liquors has already been discussed, so only the treatment of sulphide-containing effluent will be discussed here. It is common practice to keep sulphide-containing effluent from the beamhouse separate and at a high pH until the sulphide is treated, because at a pH lower than 9.0 the formation of toxic hydrogen sulphide gas can occur. The sulphides in the deliming and pickle liquors can easily be oxidised in the drum by adding hydrogen peroxide, sodium metabisulphite or sodium bisulphite. The associated emission level after treatment of sulphide is 2 mg/l in a random sample in the separate effluent. Where segregation of sulphide-bearing liquors is not possible, the sulphides are generally removed by means of precipitation with iron (II) salts and aeration. A disadvantage of this precipitation is the generation of high volumes of sludge. The levels that can be achieved in treating the mixed effluent are - depending on the mixing rate - 2 mg S²⁻/l and 1 mg Cr_{total}/l (e.g. if 50 % of the mixed effluent consist of the chrome-bearing effluent and 50 % of the mixed effluent consist of the sulphide-bearing effluent, emission levels for the total effluent will be 1 mg S²⁻/l and 0.5 mg Cr_{total}/l).

Usually the first treatment of the raw effluent is the mechanical treatment that includes screening to remove coarse material. Up to 30 - 40 % of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling. After mechanical treatment, physico-chemical treatment is usually carried out, which involves the chrome precipitation and sulphide

treatment described above. Coagulation and flocculation are also part of this treatment to remove a substantial percentage of the COD and suspended solids.

Effluent from tanneries after mechanical and physico-chemical treatment is generally easily biodegradable in standard aerobic biological treatment plants. The data in the table below represent typical values for tannery waste water treatment efficiency for conventional process liquors for production of finished leather from raw material.

Parameter % or mg/l	COD		BOD ₅		SS		Chrome mg/l	S ²⁻ mg/l	TKN	
	%	mg/l	%	mg/l	%	mg/l			%	mg/l
PRETREATMENT										
Grease removal (dissolved air flotation)	20 - 40									
Sulphide oxidation (liming and rinsing liquors)	10							10		
Chromium precipitation							1 - 10			
PRIMARY TREATMENT										
Mixing + Sedimentation	25 - 35		25 - 35		50 - 70		20 - 30		25 - 35	
Mixing + Chemical treatment + sedimentation	50 - 65		50 - 65		80 - 90		2 - 5	2 - 10	40 - 50	
Mixing + Chemical treatment + flotation	55 - 75		55 - 75		80 - 95		2 - 5	2 - 5	40 - 50	
BIOLOGICAL TREATMENT										
Primary or chemical + Extended aeration	85 - 95	200 - 400	90 - 97	20 - 60	90 - 98	20 - 50	<1	<1	50	150
Primary or chemical + Extended aeration with nitrification and denitrification	85 - 95	200 - 400	90 - 97	20 - 60	90 - 98	20 - 50	<1	<1	80 - 90	30 - 60

Post-purification- sedimentation and sludge handling are the last step in waste water treatment. With sedimentation the sludge in the waste water treatment plant is separated from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40 % dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20 – 25 % dry solids. Centrifuges achieve up to 25 – 45 % dry solids and thermal treatment up to 90 % dry solids. Energy is an important factor in these processes.

European tanneries' waste water effluent is treated in many different ways. There are situations in which an individual tannery applies all the above-described waste water treatment steps on site. In other situations an individual tannery may apply (on site) only pre-treatment or a part pre-treatment or no treatment at all, sending the effluent to a communal effluent treatment plant; these may be jointly owned and are usually dedicated to processing tannery effluent. A tannery might also treat its effluent partly on site, but then discharge to a municipal sewage works and make some financial arrangement for effectively sharing the role of effluent treatment.

Waste management and treatment

The above-mentioned process-integrated measures will directly or indirectly also prevent the arising of waste. It is also important to treat waste that cannot be prevented in such a way, e.g. by separating of specific fractions, that efficient treatment is possible. Several options for the recycling or re-use of organic waste fractions are available:

- gelatine and glue from untanned wastes can be produced; in some Member States untanned wastes are processed to produce sausage casings
- tallow recovery from raw trimmings, fleshings and splits is performed in rendering plants. Limed trimmings, fleshings and splits may need pre-treatment before conversion
- fat can be separated and recycled, but this is practicable only in exceptional cases
- recovery of protein (protein hydrolysate) from e.g. splits, for conversion into fertiliser
- recovery of collagen from e.g. lime trimmings and splits. Collagen has various uses as meat and bakery product additives, in pharmaceuticals and cosmetics, and as additives to rubber products
- tanned wastes can be used in leather fibreboard production.

Further treatment options for organic waste and sludges from waste water treatment are composting, recycling in agriculture, anaerobic digestion, landfill and thermal treatment. The applicability of the techniques in sludge disposal depends on the composition of the sludge, especially the chrome content, and has to be assessed on a case-by-case basis, taking into account national regulations and strategies.

Other residues may require further (off-site) treatment. This includes the following wastes: salt, organic solvents and chemicals used as process chemicals, auxiliaries, cleanser, sludges from finishing, solids from air abatement (activated carbon, sludges from wet scrubbers) and packaging material.

Air abatement

Releases to air can arise from various process steps carrying different substances and particulates. Preventative measures and end-of-pipe techniques are available to prevent or abate emissions from organic solvents, ammonia, hydrogen sulphide, sulphur dioxide, total particulate together with the odour which might arise from those substances.

Energy

Very little information is available on energy use in tanneries. For collecting more information it is necessary to record the energy consumption for electricity, heat (steam and heating) and compressed air, particularly for the units with highest consumption, such as waste water treatment and drying procedures.

Noise, vibrations

There is no information at all on this subject.

Monitoring

Standardised analysis and measurement techniques exist for monitoring waste water effluent parameters, but it is important to use the same units to make those data comparable. In this document data are sometimes expressed as concentrations or in relation to the leather produced or the raw hides input. This makes it very difficult to compare emission data and the performance of the techniques used. Information about the monitoring of gaseous emissions, waste, energy and noise is not available.

Decommissioning

General decommissioning operations are described, but information specific to the decommissioning of tanneries is not available.

BAT in tanning industry (Chapter 5)

Management & good housekeeping

Operation and maintenance

Commitment of tannery management is a prerequisite for good environmental performance. Technology by itself is not sufficient; it needs to go together with good housekeeping measures.

A key to good performance is awareness of the inputs to and outputs of the process with regard to the characteristics of the materials, the quantities, and their potential environmental impacts. Criteria that ensure a better environmental performance can then be taken into account as well as technological criteria that focus on the properties of the end product.

Reduction of spills, accidents, water wastage and chemical usage is achieved by the choice of appropriate techniques, good maintenance and operation control – by monitoring and adjusting process parameters – and good staff training.

BAT is to implement provisions for segregation of waste streams in order to allow for recycling of certain waste streams. These provisions include training of personnel.

Accident prevention

Chemicals used in the tannery should be stored and handled in such a way as to minimise the risk of spillages and accidents. BAT is:

- to store chemicals appropriately. Basic requirements are: separation of chemicals which could react to generate dangerous emissions; labelling and use of appropriate containers; adaptation of storage rooms and areas to provide proper ventilation and soil protection, especially for halogenated and non-halogenated organic solvents and waste containing these substances
- to implement measures such as information and training of personnel; technical provisions for safety, personal protection and organisation to minimise handling of potentially harmful agents:
 - handling and accidental spillage might lead to unforeseen chemical reactions such as, e.g., the release of sulphides
 - protection has to be provided against releases of harmful substances. To substitute organic solvents and other agents where possible
 - to ensure that Material Safety Data Sheets for all chemicals and preparations used and stored on site are available and easily accessible
- to provide first-aid facilities and to establish evacuation procedures
- to make contingency plans for avoiding shock loads to sewage treatment plants
- to monitor the operation of end-of-pipe abatement measures
- to have clean-up materials readily available for dealing with spillages
- to ensure efficient capture of waste water from clean-up operations
- to keep records of accidents and incidents.

Substitution of chemicals

For the substitution of chemicals, BAT is:

- to substitute less harmful chemicals for agents and auxiliaries that are known to be harmful to the environment
- to maintain an inventory of inputs and outputs, their fate in processes and releases
- to measure appropriate parameters to monitor the environmental releases
- to exercise responsible management including e.g. awareness of the chemicals applied in the process (including ready-made supplies), staff training, information and safety measures for workforce and environment.

In Table 5.1, substances to be substituted are listed in the left column. BAT substitutes are listed in the right column.

SUBSTANCE	BAT SUBSTITUTE
Biocides	<ul style="list-style-type: none"> • Products with the lowest environmental and toxicological impact, used at the lowest level possible e.g. sodium- or potassium-di-methyl-thiocarbamate
Halogenated organic compounds	<ul style="list-style-type: none"> • They can be substituted completely in almost every case. This includes substitution for soaking, degreasing, fatliquoring, dyeing agents and special post-tanning agents - Exception: the cleaning of Merino sheepskins
Organic solvents (non-halogenated) The finishing process and the degreasing of sheepskins are the major areas of relevance.	Finishing: <ul style="list-style-type: none"> • Aqueous-based finishing systems - Exception: if very high standards of topcoat resistance to wet-rubbing, wet-flexing and perspiration are required • Low-organic solvent-based finishing systems • Low aromatic contents Sheepskin degreasing: <ul style="list-style-type: none"> • The use of one organic solvent and not mixtures, to facilitate possible re-use after distillation
Surfactants APEs such as NPEs	<ul style="list-style-type: none"> • e.g. alcohol ethoxylates, where possible
Complexing agents EDTA and NTA	<ul style="list-style-type: none"> • EDDS and MGDA, where possible
Ammonium deliming agents	<ul style="list-style-type: none"> • Partially with carbon dioxide and/or weak organic acids
Tanning agents - Chromium - Syntans and resins	<ul style="list-style-type: none"> • 20 – 35 % of the fresh chrome input can be substituted by recovered chrome • products with low formaldehyde, low phenol and low acrylic acid monomer content
Dyestuffs	<ul style="list-style-type: none"> • De-dusted or liquid dyestuffs • High-exhausting dyes containing low amounts of salt • Substitution of ammonia by auxiliaries such as dye penetrators • Substitution of halogenic dyes by vinyl sulphone reactive dyes
Fatliquoring agents	<ul style="list-style-type: none"> • Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • High-exhausting to reduce the COD as much as possible
Finishing agents for topcoats, binders (resins) and cross-linking agents	<ul style="list-style-type: none"> • Binders based on polymeric emulsions with low monomer content • Cadmium- and lead-free pigments and finishing systems
Others: - Water repellent agents - Brominated and antimony-containing flame retardant	<ul style="list-style-type: none"> • Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • Free of metal salts - Exception: waterproof leathers • Phosphate-based flame retardants

Table 5.1: BAT for the substitution of chemicals

Process-integrated BAT measures

With the implementation of BAT in the process rather than choosing an end-of-pipe abatement, improvement is gained with regard to:

- consumption of chemicals
- substitution of hazardous chemicals by less hazardous ones
- water and waste management
- emissions to air
- energy savings.

It is therefore essential in selecting BAT that the equipment used, e.g. processing vessels, the dosage of chemicals and the process control devices are also examined for their efficiency and compatibility with the above-mentioned goals. These pre-requisites are also discussed in the section on Management & Good housekeeping

Table 5.2: (Process-integrated BAT Measures) describes BAT – where possible – for every separate process unit in a tannery. In two cases no consensus was reached in the TWG.

The first case is the recycling of the pickle liquor. Spent pickle liquors from the pickling process can be recycled into the pickling process or be re-used in the tanning process in order to reduce the amount of salt and effluent discharged to sewer. Experts representing one Member State and some experts representing industry in the TWG did not fully support this view, because it can have a negative effect on the quality of leather, especially aniline leather. A split view is recorded.

The second case is about chrome tanning. The majority of the TWG agreed that the best available technique for chrome tanning is to increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed, all in combination with chrome recovery through precipitation for waste water streams containing total chrome > 1 g/l. They also agreed that, when chrome recovery is not possible (either individually or in a common plant), then high-exhaustion tanning methods are the best-performing alternative. Experts representing one Member State and some experts representing industry do not fully support this BAT. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for a large part of the European leather industry, particularly in situations where a common specialised treatment plant is not available. Although they agree that BAT is to increase the efficiency, they assert that chrome recovery cannot be BAT when common specialised recovery plants are not available. Nor, in their view, can chrome recovery be BAT when the recovered chrome cannot be recycled into the tanning process. This is the case when high quality leathers are produced, because high quality leather can only be produced with "fresh" chrome, not with any addition of recovered chrome or with high-exhaustion chrome tanning agents. In their view, chrome recovery is not economically viable in this situation. A split view is recorded.

	PROCESS UNIT	BAT is:
BEAMHOUSE	Curing and soaking	<ul style="list-style-type: none"> To process fresh hides as far as they are available <p>Exceptions:</p> <ul style="list-style-type: none"> When long transport time is necessary (max 8 - 12 hours for fresh, unchilled hides; 5 - 8 days if a cooling chain of 2 °C is maintained) For certain types of end-products Sheepskins, calf skins <ul style="list-style-type: none"> To reduce the amount of salt used as far as possible.
	Unhairing & liming	<ul style="list-style-type: none"> To use hair-save technology, but economics can be an issue for existing plants when re-use of the saved hair is not possible To reduce sulphide consumption by the use of enzyme preparations; not for sheepskins To recycle spent liquors only when processing sheepskins, which are dewoolled by painting
	Splitting	<ul style="list-style-type: none"> To use lime splitting <p>Exceptions:</p> <ul style="list-style-type: none"> When the starting material is wet blue When a firmer leather has to be produced (e.g. shoe-leather) When a more uniform and accurate thickness is needed in the final product <ul style="list-style-type: none"> To maximise the use of split
TANYARD OPERATIONS	Deliming and bating	<ul style="list-style-type: none"> To make a partial substitution of ammonium salts with CO₂ and/or weak organic acids
	Sheepskin degreasing	<ul style="list-style-type: none"> To optimise wet degreasing using surfactants, with or without organic solvents Closed machines with abatement for air and waste water releases when organic solvents are used to degrease skins in dry state
	Pickling	<ul style="list-style-type: none"> To use partial recycling or re-use of pickle liquors (*) split view; see below To use a volume of floats in the range of 50 – 60 % (based on fleshed weight) for ovine skins and bovine hides in order to reduce salt consumption
	Tanning (**) split view; see below	<ul style="list-style-type: none"> To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed, all in combination with chrome recovery through precipitation for waste water streams containing Cr_{total} > 1 g/l (**) To use high-exhaustion tanning methods where chrome recovery is not possible (**) To maximise exhaustion of the vegetable tanning liquor with counter-current (pit system) or recycling (drum tanning)
POST-TANNING OPERATIONS	Retanning, chrome fixation and neutralisation	<ul style="list-style-type: none"> To enhance exhaustion of post-tanning treatment agents and fixation of tanning agents in the leather To reduce the salt content of spent liquors
	Dyeing	<ul style="list-style-type: none"> To enhance exhaustion of dyestuffs
	Fatliquoring	<ul style="list-style-type: none"> To enhance exhaustion of fatliquor
	Drying	<ul style="list-style-type: none"> To optimise mechanical dewatering prior to drying where possible
	Applying a surface coat	<ul style="list-style-type: none"> To use roller coating To use curtain coating To use HVLP spray guns To use airless spray guns <p>Exception for all four above-mentioned techniques:</p> <ul style="list-style-type: none"> When very thin finishes are applied, e.g. on aniline and aniline-type leather
<p>(*) split view on Pickling: The majority in the TWG agreed that partial recycling or re-use of pickle liquors is BAT. Experts representing one Member State and some experts representing industry in the TWG did not fully agree because in their view an exception has to be made. In their view BAT is:</p> <ul style="list-style-type: none"> To use partial recycling or re-use of pickle liquors with an exception for high quality leathers. <p>(**) split view on Tanning: Experts representing one Member State and some experts representing industry do not fully support this BAT. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for a large part of the European leather industry, particularly in situations where a common specialised treatment plant is not available. In their view BAT is:</p> <ul style="list-style-type: none"> To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drumspeed To use chrome recovery through precipitation Exceptions: - When common specialised recovery plants are not available - When the recovered chrome cannot be recycled in order to produce high quality leathers To use high-exhaustion tanning methods Exception: - High quality leather production. 		

Table 5.2. Process-integrated BAT measures

Water management and treatment

BAT for water management and treatment comprises:

- reduction of water consumption
- good housekeeping
- process-integrated measures (listed in Table 5.2) and, finally,
- effluent treatment.

Within these areas, BAT is:

GOOD HOUSE-KEEPING AND PROCESS - INTEGRATED MEASURES	To improve the matching of water flow to the requirements of the process
	To use 'batch' versus 'running water' washes
	To modify existing equipment to use short floats
	To use modern equipment for short floats
	To re-use waste water in less critical processes
	To recycle or re-use process liquors where possible (see Table 5.2)
EFFLUENT TREATMENT	To keep sulphide-containing effluent from the beamhouse separate and at high pH until the sulphide is removed. The associated emission level after treatment is 2 mg S ²⁻ /l in a random sample in the separate effluent. After the sulphide is removed (on site or in a jointly used dedicated treatment plant) the effluent can be mixed. (***) split view; see below.
	To collect chromium-containing partial effluent (e.g. from tanning and samming) with a concentration of Cr _{total} > 1 g/l separately and send it for chrome recovery. Chrome recovery can be done on or off site (****)
	To treat (on or off site) chromium-containing effluent with a concentration of Cr _{total} < 1 g/l in combination with other effluent (****)
	To use mechanical treatment (on or off site)
	To use biological treatment (on or off site)
	To use post-purification sedimentation and sludge handling (on or off site)
<p>(****) split view on sulphide and chromium treatment: Industry supports the conclusion that separate treatment of sulphide-containing effluent is BAT, but in their view the mixed treatment – on site – of sulphide- and chrome-containing effluent is also BAT. The arguments are the following:</p> <ul style="list-style-type: none"> • lower costs • less chemicals have to be used • the technique is simple and reliable • emission levels for the total effluent – depending on the mixing rate – of 2 mg S²⁻/l and 1 mg Cr_{total} /l can be achieved. (e.g. if 50 % of the mixed effluent consist of the chrome-bearing effluent and 50 % of the mixed effluent consist of the sulphide-bearing effluent, emission levels for the total effluent will be 1 mg S²⁻/l and 0.5 mg Cr_{total} /l). <p>(****) see split view on chrome recovery in note (**) on Table 5.2 and see split view on separate treatment in note (***) on this table.</p>	

Table 5.3: BAT for water management and treatment

For all the techniques mentioned in Table 5.3, it has to be decided site-specifically whether primary, secondary or even tertiary treatment is more environmentally and economically efficient on site or in a jointly used dedicated waste water treatment plant. It can also be efficient for a tannery to treat its effluent partly on site and then discharge it to a municipal sewage treatment works. The removal of particular substances from the waste water effluents e.g., biocides, halogenated organic compounds, surfactants and other process agents that need specific treatment, also has to be decided on a case-by-case basis.

Waste management and treatment

In waste management and treatment, BAT, in order of priority is:

- prevention
- reduction
- re-use
- recycling / recovery
- thermal treatment for certain types of waste.

Landfill is not BAT, although in some cases it is the only option available.

A large amount of waste, in particular organic waste, is inherent to production in tanneries. Both organic waste fractions and other residues can be prevented and reduced to a large extent by using BAT in the process units. Recycling options are numerous and carried out on site and off site. The potential for recycling should be exploited by ensuring segregation of waste. Of equal importance is commercialisation of wastes as by-products and co-operation between tanners to make recycling and re-use options economically feasible.

Waste that arises in the tannery has to be handled and stored in such a way as to avoid leaching, odour problems and emissions to air.

In Table 5.4 re-use, recycling / recovery and treatment options are given in the first column and waste fractions that can be used for the respective option are listed in the second column. BAT is to identify opportunities to implement these measures where feasible, ensuring that actions are carried through.

Re-use / recycling / recovery and treatment	Type of waste
Leather production	Splits
Leather fibre board production	Tanned wastes in general, e.g., splits, shavings, trimmings
Small leather goods etc.	Splits and tanned trimmings
Filling material, wool	Hair and wool
Gelatine and/or hide glue	Raw trimmings, green and limed fleshings and splits
Sausage casings	Untanned splits
Fat recovery	Raw trimmings, green and limed fleshings
Protein hydrolysate	Hair, raw and limed trimmings, green and limed fleshings, green, limed and tanned splits and shavings
Collagen	Limed trimmings and splits
Agriculture and fertiliser	Hair for the nitrogen content, residues from composting and anaerobic digestion, sludges from waste water treatment. The legal requirements for the application of waste to land require sophisticated waste separation and treatment of the various fractions
Composting	Hair, green and limed fleshings, green, limed and tanned splits and shavings, fats, grease and oil; sludges from waste water treatment
Anaerobic digestion	Hair, raw trimmings, green and limed fleshings, green, limed splits, fats, grease and oil; sludges from waste water treatment
Thermal treatment	Fats, grease, mixtures of non-halogenated organic solvents and oil
Recycling of organic solvents	Organic solvents (no mixtures)
Regeneration of air abatement filters	Activated carbon filters
Re-use and recycling of packaging material by feeding it back to the supplier via an appropriate recycling system	Container, pallets, plastic, cardboard

Table 5.4: BAT for waste management

Air abatement

BAT is to prevent the generation of odours through process control, maintenance and proper handling and storage of raw hides and wastes, in some cases requiring the installation of filters, e.g. at waste water treatment plants or for VOC releases.

BAT to prevent releases of e.g. hydrogen sulphides, ammonia, VOCs and dust, are mentioned in Table 5.1, Table 5.2 and/or Table 5.3. In addition, the following end-of-pipe measures are BAT for the abatement of hydrogen sulphides, ammonia and VOCs in particular:

- wet scrubbing, for example, to abate ammonia and hydrogen sulphides from deliming, pickling and dyeing
- wet scrubbing, absorption, bio-filters, cryogenic removal or incineration to abate VOC from degreasing, drying and finishing
- wet scrubbing, absorption or bio-filters to abate various releases from waste water treatment.

Techniques exist that are suitable for the abatement of a combination of releases, e.g. wet scrubbing for removal of aerosols, organic solvents and odours. Too little information is available to come to detailed conclusions on BAT.

Energy

BAT is to record the energy consumption for electricity, heat (steam and heating) and compressed air, particularly for the units with the highest consumption, such as waste water treatment and drying procedures.

Operators therefore need a system for monitoring energy usage and performance. The scale of this needs to match the level of energy usage, but the following activities should be considered:

- recording actual energy usage, split by energy type and major end-uses, on a specified and appropriate regular basis (e.g. hourly, daily, weekly, etc.)
- generating energy performance indicators (historical energy performance or normalised to an indicator of production/external temperature/building occupancy etc.)
- monitoring energy performance, including mechanisms to alert the operator to significant variations from predicted energy performance
- ensuring appropriate investigative and corrective action is taken, and recorded, in response to variations
- delivering concise, appropriate and timely energy performance information to all individuals with identified responsibilities for energy management
- setting, reviewing and revising performance targets.

Too little information is available to come to detailed conclusions on BAT.

Decommissioning

In general, BAT for decommissioning of a tannery includes all provisions and measures that have to be taken into account to prevent environmental impact during and after the shut-down process. The aim is to prevent impact on the environment in general, and in particular the immediate surroundings, by activities that have to be carried out to leave the area in such a way that it can be re-used (depending on the enforcement bodies' decision on land use planning). This includes activities from the shut-down of a plant itself, the removal of buildings, equipment, residues etc. from the site, and contamination of surface water, groundwater, air or soil. Too little information is available to come to detailed conclusions on BAT.

Concluding remarks (Chapter 7)

Level of consensus

This BREF has met support from most of the TWG members, although on three BAT conclusions the following split views had to be noted:

1. The majority in the TWG agreed that partial recycling or re-use of pickle liquors is BAT, but experts representing one Member State, and some experts representing industry in the TWG, did not fully agree. In their view BAT is to use partial recycling or re-use of pickle liquors with an exception for high quality leathers.
2. Experts representing one Member State and some experts representing industry do not fully support this BAT conclusion on chrome recovery. Their opinion is that a separate treatment of chrome-containing liquors is not currently economically viable for many individual tanneries where a common specialised treatment plant is not available.
3. Industry supports the conclusion that separate treatment of sulphide-containing effluent is BAT, but in their view also the mixed treatment – on site – of sulphide- and chrome-containing effluent is BAT.

Recommendations for future work

For future BREF reviews, all TWG members and interested parties should continue to collect data on the current emission and consumption levels and on the performance of techniques to be considered in the determination of BAT. For the review, it is also important to collect more data on the achievable emission and consumption levels and the economics of all tanning processes and tanning agents. Information on reference plants and actual performance data are also scarce; for the revision of this document the missing information should be provided. Apart from these general areas, mention have been made in the body of the BREF of more specific areas in which data and information are lacking.

Recommendations for future R&D work

The previous paragraph highlights many areas for attention in future work. Much of the future work concerns the collecting of information to be used in reviewing this BREF. Proposals for future R&D work focus on the techniques that are identified in this BREF, but are too expensive or cannot be used yet because of the high risk of damaging the hides, the skins and/or the leathers. Proposals for future research into new techniques for tanneries, including those relevant to water and sludge, solid waste, air and soil are also addressed in Chapter 7.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).