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Solid wastes and sludges

The most effective ways to minimise the problem presented by solid waste and sludges are:

• REDUCE WASTE AT SOURCE

Ensure that the raw hides and skins are appropriate for the end purpose. Apply rationalised processing using pre-fleshing, lime splitting, pre-tanning/splitting/shaving wherever possible for optimum chemical application to the substrate, and minimum contamination of solid waste. Ensure that the yields from splitting and shaving as valuable leather are as high as possible. Minimise waste in the form of unusable splits, shavings and trimmings.

• VIEW BY-PRODUCTS AS POTENTIAL RAW MATERIALS

Segregate major by-products wherever possible—green fleshings, hair from hair recovery processing, wastes from pre-tannages or tannages that can biodegrade, chrome for recovery. There are many outlets for these by-products and, as the costs of disposal rise, or legislation becomes more stringent, these options become more cost effective.

• SELECTIVE MANAGEMENT OF SLUDGES

Separate chrome-containing sludges from those that can biodegrade.

By-products as new raw materials

Many by-products are produced during leather manufacture. Often viewed as waste these include:

SALT: Although not common practice, salt recovered following the rationalised evaporation of segregated soak liquors is being reused in the pickling process.

FLESHINGS: Fleshings are best uncontaminated by any chemicals, so that extracted fats may find uses within industry. If contaminated, extracted greases can be used as boiler fuel. Other uses include drying and grinding as poultry feed, fertilisers and digestion for bio-gas production.

HAIR: Most recovered hair is felted, and cannot be used within fabrics. However, it is being used in forming biodegradable plant pots, and when blended with compostible materials hair is being broken down for soil conditioning. It is being digested within bio-gas production, and alkaline treatment can produce a hydrolysate.

LIMED SPLITS: Apart from use as split leathers, and potential uses as leather/laminate composites, outlets are found as collagen, casings and gelatin. Simple technology can also add value as dog-chew products.

PRECIPITATED CHROME: Used chrome liquors can be readily precipitated to form a sludge containing chromium hydroxide, dewatered, then regenerated and reused as chrome tanning

material. Contaminated chrome has also been used in the manufacture of firebricks.

SPLITS AND SHAVINGS: The prime use for splits is for leather or leather/laminate composites. However, there is waste in the form of unusable trimmings.

From pre-tanning systems: if the materials have not been committed to a major tanning process, then the waste can be composted, hydrolysed, or used for bio-gas production.

From chrome tannage: There are two main outlets for use:

- Chrome shavings and splits can be mascerated, mixed with latex and resin blends, and formed into sheets of leather board. This product can be used in footwear construction, finished for use in belts and travel cases, or moulded for components in the auto sector.
- The shavings are mixed with lime and water, then heated to form a slurry. This is filtered to remove an impure form of chromium hydroxide, and the hydrolysate concentrated to either a viscous solution or dry solids. Uses for this product include adhesives, new copolymers and retanning agents, foam generation, hog feed, but mainly as (grass) nutrient.

LEATHER TRIMMINGS AND OFF-CUTS: Considerable volumes are used for small leather goods, segments for industrial gloves, key fobs, mobile phone cases, etc. Very small pieces of dyed splits, and thin grain leathers, are cut and stitched together into rectangular sheets, then used for bags and purses.

Addressing biodegradable sludges

Chrome-free sludges, following coagulation with ferric compounds from primary treatment, and secondary sludges, are being mixed with vegetable matter and composted before land application as a conditioner. This process has been operated successfully on a very large scale in conjunction with farming for many years, and there are other examples.

Sludges from municipal effluent treatment have been injected into the ground for growing willow for gasification purposes. Similarly, sludges from fresh hides to wet blue manufacture are being directly injected into the ground as fertiliser. Hair burning techniques are being used with careful chemical selection and control, chrome recovery, and measures to minimise salinity. In this situation crop yield have increased.

If dried, these sludges, and other chrome-free waste and leathers, can also be incinerated.

Chrome-containing sludges and solid waste

Legislation concerning land application of chrome-containing sludges to the ground varies. Limits are set for deposit as chromium, but together with many other products these limits are likely to become more stringent. In general, these are being disposed of in landfill sites, but alternative treatment is being ►



Panel 9

Developing technologies for wastewater treatment

Membrane Applications

Membrane applications for chemical recovery within the tannery, rationalisation of effluent treatment, and water recovery have been extensively studied. The potential advantages include economic and logistical benefits of chemical use reduction, water savings and discharge compliance.

With most membrane types, the feed passes at high velocity within a tubular membrane, which under slight pressure causes the permeate to pass via the pores of the membrane. Larger particles are retained and concentrated, with a corresponding fall in concentration in the permeate. The pore size denotes the composition of the permeate produced and pressures required for effective separation. Specific chemicals may thus be physically separated, concentrated and recovered, even from very dilute waste streams.

Concentration and separation is achieved without a change of state and without use of chemicals or thermal energy. The process is energy efficient and ideally suited for recovery applications.

Many process liquors can be reused, especially following 'top-up' of chemical concentration levels. Reported applications include the recycling of water from soak liquors, sulfide from unhairing liquors, water and surfactant recovery from aqueous degreasing, pickle liquor recovery from chrome tanning liquors, and direct vegetable tanning liquor reuse.

Membrane Bioreactors, as a development of the activated sludge

process, are already in operation. High COD and BOD removal rates and efficiencies (90% and 99%) are noted in addition to an extremely low excess sludge production. This is due to the long retention of both biomass and the large molecules within the effluent for treatment.

Effluent for crop irrigation

Many components within effluents have value in agriculture, and are found in fertilisers. Where water is in short supply and there is pressure on finding uses for 'grey waters,' many tanneries are applying primary treatment only, then use the part-treated effluent for crop irrigation. This approach is mainly taking place in Australia where the technique is long established and proven in value. The presence of common salt is the major obstacle to this approach, so hides must be fresh, with a strong focus on clean manufacture to minimise salinity. In addition, there must be a minimisation of chrome or aluminium content. Close attention is needed to achieve the correct nutrient balance in line with crop needs and storage to manage grey water use and thus avoid water logging. Providing the land is available, this is a powerful alternative to full wastewater treatment.

Similarly, tannery effluents are being used for irrigation in India. At one CETP, the effluent is being used for irrigation in a mini forest where woods of value are being grown, with no effluent being discharged from the site. At another location woodlands are being irrigated, and flowers of commercial value being grown.

investigated. This is to minimise the organic content within deposited wastes, and to either make better use of chromium compounds, or to lock them in an inert form.

Thermal processing

Simple incineration cannot be used, as combustion with the normal excess of oxygen can convert some of the chrome from the trivalent to hexavalent state. However, these solids and wastes can be degraded by pyrolysis, and release a considerable amount of energy as heat and combustible gases.

In this event, the pre-dried sludge is first roasted in the absence of oxygen producing water, tars, hydrogen, carbon monoxide, methane and light hydrocarbons as a vapour. A residual char is also produced comprising mainly carbon and inorganic residues.

In a second stage this char can be consumed with a limited amount of oxygen, undergoing a series of oxidation and reduction processes to produce hydrogen, carbon monoxide and methane as combustible gases. Different operating conditions—temperature, oxygen and time—can produce different ratios of gases and condensates.

There are many variations of this process. The two stages can take place in two converters, or in a single reactor. The sludge can be presented as a pressed cake, blended with other materials—fleshings, hair, chrome shavings, trimmings, pallets, plastics, domestic waste, etc.—and ground/flash dried before entering the first phase. Alternatively, the feed can be dried, then compressed into briquettes before offer to the reactor.

In some configurations, the char can be removed for alternative uses. Where blends are used, a mixture of molten slag and metals including chrome can be tapped from the base of the

reactor. If glass is added to the blend, the chrome oxide, other metals, or potential leachates may be locked in a fused slag. If leather shavings are used, an ash rich in Cr_2O_3 is produced with potential for chrome regeneration.

Where other outlets are not an option, the gasification process appears the ultimate solution to tannery waste, even leather goods at the end of a useful life. Benefits may include energy as surplus heat, a distillate as fuel oil and combustible gas, and the technology is proven.

Ashes can be fused, but if chrome recovery is required the avoidance of Cr(VI) must be paramount. There are possibilities of ash containment +/- reduction, but in any event the process must be environmentally secure.

Solid waste and landfill

The landfill option for solid waste is under increasing pressure due to land shortages, rising costs and increasingly stringent legislation. Where this route is being followed, there is a need for careful site management and attention to construction. This includes membranes, concrete or clay linings for security and to prevent contamination from run-off. Leachate requires treatment as effluent, and may need specialised attention. 

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Annex to Back to Basics Environmental
(to appear in early 2005 issues)

The annex will provide synopses of technologies central to this study, with references to pertinent papers and articles previously published in World Leather. Associated matters that deserve greater expansion, such as clean technology and energy conservation, will be included forming a comprehensive guide for the leather sector regarding environmental matters.