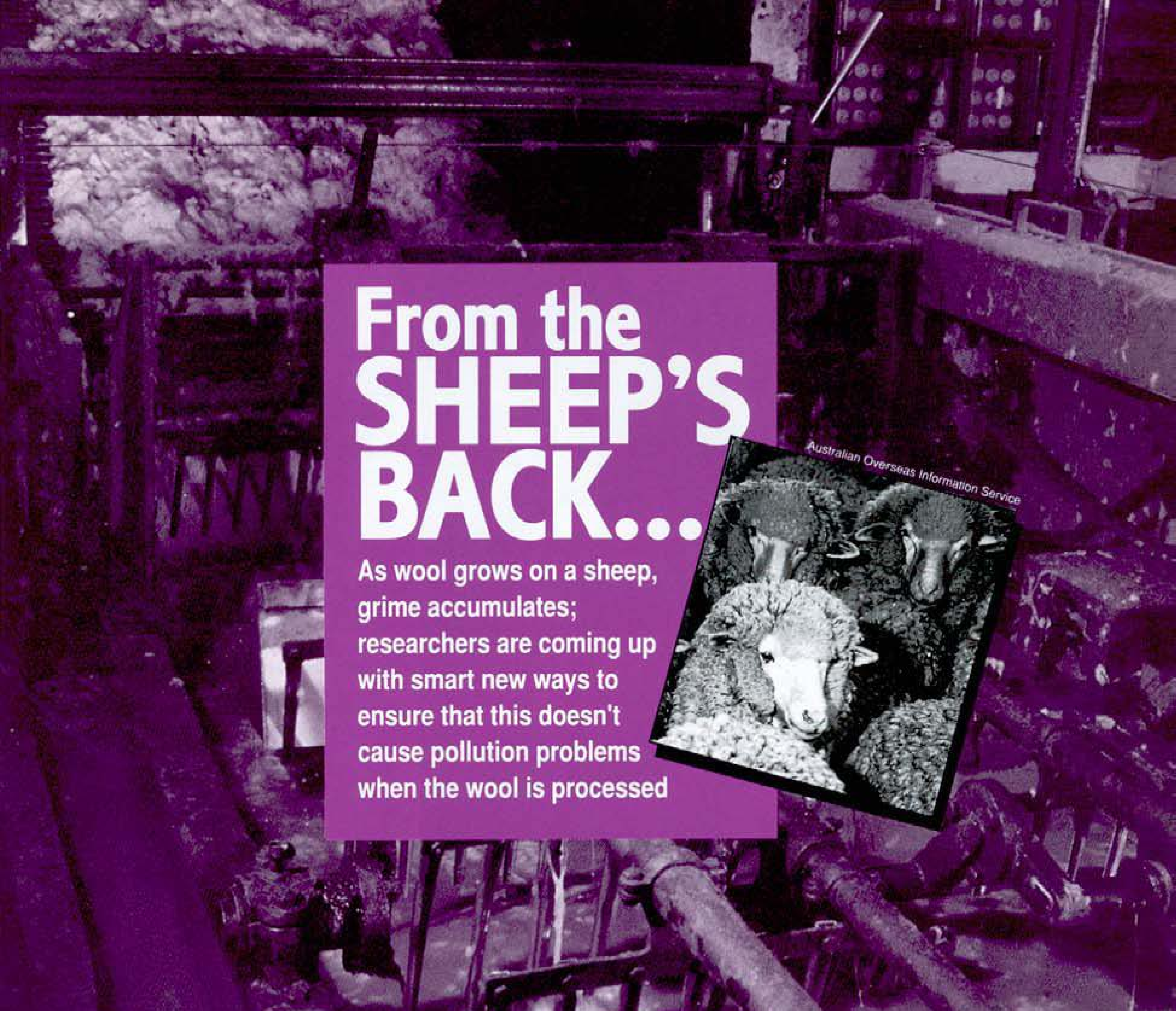
From the SHEEP'S BACK...

As wool grows on a sheep, grime accumulates; researchers are coming up with smart new ways to ensure that this doesn't cause pollution problems when the wool is processed



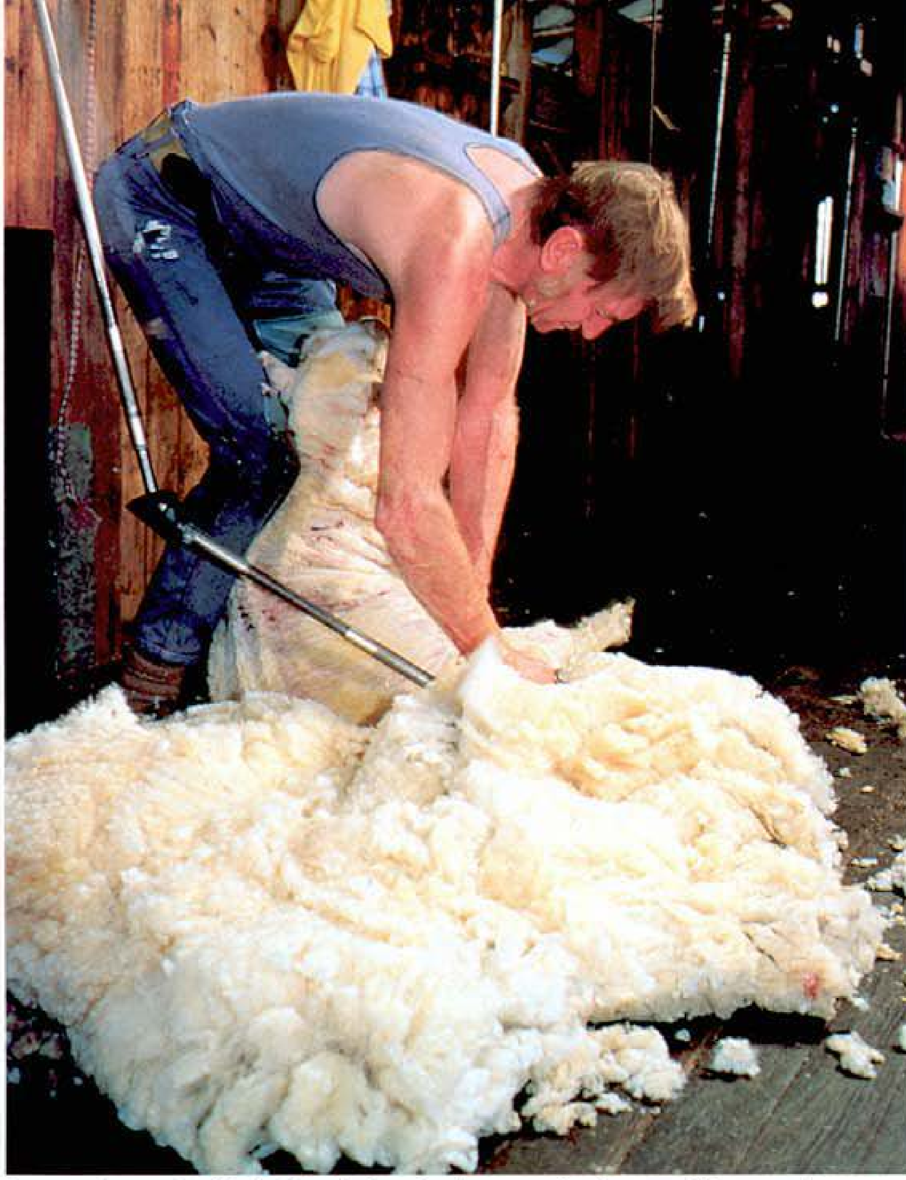
Wool scouring in progress.

The wool came safe and is sold but to great disadvantage owing to the very dirty state it is in. — **John Macarthur to his wife, Elizabeth, on their first commercial shipment of Australian wool in 1813.**

The wool industry is a dirty, thirsty business. Australia might have ridden for many decades on the sheep's back, but so did a lot of muck, grime and parasites. As much as two-thirds of the weight of raw, unwashed wool can comprise grease, dried sweat, skin flakes, dirt and vegetable matter, and getting wool clean or scoured requires billions of litres of water, detergent and chemical solvents. In addition, nearly $60 million worth of chemical pesticides are sprayed onto sheep each year to control lice and flies.

Increasingly, woolgrowers and processors recognise the potential problems an economic activity as large as the wool industry poses for the environment. In the past 40 years considerable research and development has occurred on environmental issues associated with wool, resulting in an industry that is cleaner today than at any time in its long history. The industry now spends several million dollars a year on environmental research — an investment sharply at odds with the attitudes and practices of wool's early history.

Washing sheep to improve the value of their wool was among Australia's earliest polluting industries. Early 19th century graziers undertook 'brook-washing' (a term sometimes used to distinguish the practice from washing scabby sheep with a tobacco extract) by damming a nearby creek, herding the sheep into the growing lake and pressing out the dirt by hand. Due to the greasiness of the fleece, results were poor. The historians John Garran and Les White colourfully described the practice as being only 'marginally more intelligent than milking a cow by having one person hold the teats, while four more lift the animal up and down.' Cold-water sheep-washing was quickly followed by the use of warm



Australian Overseas Information Service

Once graziers washed their sheep before shearing; now the shorn wool is scoured.

water and soap in makeshift baths, and finally the use of hot water, soap and other chemicals on shorn wool, so beginning the factory process of wool scouring.

Early wool-processing efforts were, to say the least, environmentally insensitive because of the amount of water they consumed and the huge quantities of organic waste they discharged into rivers and creeks. In Victoria last century, one sheep-wash plant alone was estimated to have required 400 gallons of water a minute to supply just one running spout. The first solvents used in wool scouring included stale urine and soda. The effluent discharged from the phalanx of wool-processing factories and dyeworks along the river banks helped turn Melbourne's two main rivers — the Yarra and the Maribyrnong — into open sewers.

Today the industry is very different, but the potential for environmental hazards from processing wool is still with us. In the long journey from the sheep's back to a finished wool product, wool undergoes dozens of chemical and physical processes that have implications for the health of workers and the environment at large. Wool scouring, for example, has become much more sophisticated and environmentally sound than it was 100 years ago, but it remains potentially a highly polluting operation that makes a growing demand on sewage treatment works.

A modern-day wool scouring mill (with two scouring machines) using aqueous detergents can produce, in terms of organic waste load, the pollution equivalent of a small city of 60 000 people. Nationally, the scourers each year consume about 2·5 billion litres of water and 1500 to 2000 tonnes of detergent — much of which can later biodegrade into compounds more toxic than the parent detergent. Typically this waste is discharged to sewers, but not all of it; thousands of cubic metres of wool-scour and textile effluent are used to irrigate land.

Further down the line, too, occupational health and environmental issues are at stake. Processors use volatile and toxic solvents such as hexane and perchloroethylene to clean and finish wool, and poisonous metal salts such as dichromate to dye wool and tan woolskins. A major dyeworks also consumes as much as 800 million litres of water a year. The use of powerful chemicals may be encountered at several stages of processing — chlorine gas, zinc and manganese compounds for shrinkproofing wool, phosphates and peroxides for fabric printing and bleaching, fluorides for flameproofing, and chlorine-based and pyrethroid compounds for mothproofing. In addition, early stages of the wool processing industry are contaminated with low levels of the pesticides used on sheep and heavy metals from the soil.

The need to safely manage the use of these chemicals and their disposal and continuing demands by the public and regulators for cleaner production technologies have prompted increasing research and development. Consequently, researchers in CSIRO are devoting more of their research effort to developing methods for the removal or avoidance of undesirable chemical residues in wool products and effluent, the minimisation of waste water and organic wastes produced by the wool industry and the proper assessment of sewage-treatment systems in relation to wool processing.

In recent years, successes include: a high-performance biological reactor for treating scouring effluent; a technique for removing pesticide residues from wool grease and lanolin; a recycling system for reducing the level of chromium in wool-dyeing effluent; a technique for tracking scouring waste in sewage; and alternatives to the use of chlorine in wool shrinkproofing. Research is also continuing on finding alternatives to chromium in woolskin tanning, safer mothproofing agents, a modified Sirolime process for removing wool from pickled sheep pelts and a vaccine against sheep lice. Much of the detail of the research remains subject to commercial-in-confidence provisions.

Synthetic dyes based on chromium have been used in wool-dyeing for more than 100 years, and have proved virtually indispensable for producing coloured fabrics in heavy shades of brown, black and navy blue that resist fading in the wash. Chromium exists in two main oxidation states: Cr(III), an essential biochemical for most organisms that occurs naturally in air and surface water at very low levels (typically less than 2 parts per billion); and Cr(VI), a proved carcinogen and source of con-

Scouring removes the grease from the wool; the scourer must then deal with the process effluent in an environmentally acceptable way.

Australian Overseas Information Service

cern among medical researchers and environmentalists for at least 30 years. Chrome-dyed wool contains only Cr (III), although effluent from the dyeing process may contain small amounts of Cr(VI). Regulatory authorities in Australia restrict the discharge of effluent containing chromium to between 1 and 20 parts per million (p.p.m.), and the indications from overseas are that the limits will get tighter. Already some European countries have emission limits as low as 0·1 p.p.m.

The future of wool-dyeing may depend, therefore, on the development of very-low-chrome dye methods. According to Dr David King and Dr Rex Brady, at the CSIRO Division of Wool Technology in Geelong, a technique they have recently developed for recycling dye liquors may hold the solution. In a conventional dyeing plant, fabric is first dyed in a bath, then acid and a chromium mordant (agent that fixes the dye to the fabric) are added to form a permanent dye complex or 'lake'. The chromium is trapped within the fibre. The exhausted dye liquors are then discarded and the bath replenished for the next fabric batch.

Initially, the chromium concentration in the dye bath may range from about 250 to 1000 p.p.m., but careful control of chemicals, pH and contaminants in the wool makes it possible to lower the level of chromium in the spent dye liquors to about 1 p.p.m.. Going lower than 1 p.p.m., however, is difficult, owing to the tendency of the wool to dissolve slightly in the dye bath, thereby keeping some of the chromium in solution.

In a preliminary trial, Dr King and Dr Brady showed that the spent dye liquors could not be left in the bath and simply 'topped up' with fresh chemicals. The repeated addition of acids and alkalis, needed to change the acidity of the bath for the dyeing and mordanting steps, eventually forms a 'buffer solution' that resists further changes in pH. Without effective control of pH, the consistency of the dyeing results quickly deteriorates.

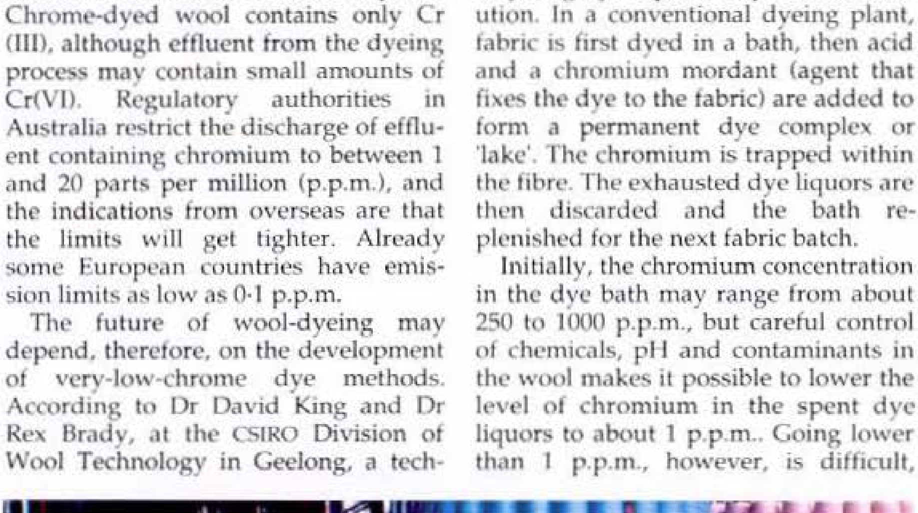
To overcome the problem, the two researchers devised a simple two-bath system that can achieve much lower levels of residual chromium without apparent loss of quality. In their system, the fabric is first treated in the bath with the dye chemicals (dye, acid, etc) without the chromium. The bath is then drained before the chroming liquor is added from a holding tank. After the fabric has absorbed the chromium compound, the spent liquor is pumped back into the holding tank, and the bath rinsed out with water. Fresh chrome is continually added to the holding tank.

By the simple act of separating the chromium compounds from the other chemicals in the process, the scientists found that they can lower the chromium concentrations in the rinse liquor to between 0·05 and 0·2 p.p.m., 10 to 15 times lower than the level in the exhausted chrome liquor using the conventional one-bath system. Even when the residual metal concentration in the bath exceeded 2 p.p.m., very low chromium levels were still possible in the rinse liquors. And yet recycling appears to make no compromise on dyeing quality, maintaining high levels of colour-fastness after 25 cycles.

The scientists believe that, by centrifuging the fabric prior to rinsing, processors can reduce the chromium level in the rinse liquor even further. The experimental technique is likely to be trialled overseas later this year by the International Wool Secretariat.

Chromium presents a potential environmental hazard in a second area — the tanning of woolskins. Although a relatively small industry here (fewer than 8% of Australia's sheepskins are tanned locally), business has been growing, and more than 20 woolskin tanneries are currently in operation.

Producing a leather that resists heat, light and washing, chromium is a cheap and excellent tanning agent.



Low-temperature dyeing.

Division of Wool Technology

Extensive research by CSIRO's Leather Research Centre in Melbourne suggests, however, that aluminium could replace it in some leather products. In particular, researchers believe aluminium could find commercial application in the making of white washable woolskin products such as car seat covers. In these products, the wool tips can — after exposure on the sheep to sunlight — become stained when later tanned with chromium products.

A team of CSIRO researchers headed by Dr Ken Montgomery has identified a number of chemical groups that can be used in aluminium tannage and has experimented with several processes. To date, the processes developed have limitations, such as high cost or instability in dyeing. Dr Montgomery says a further problem to be addressed is that some aluminium salts themselves are toxic to aquatic life.

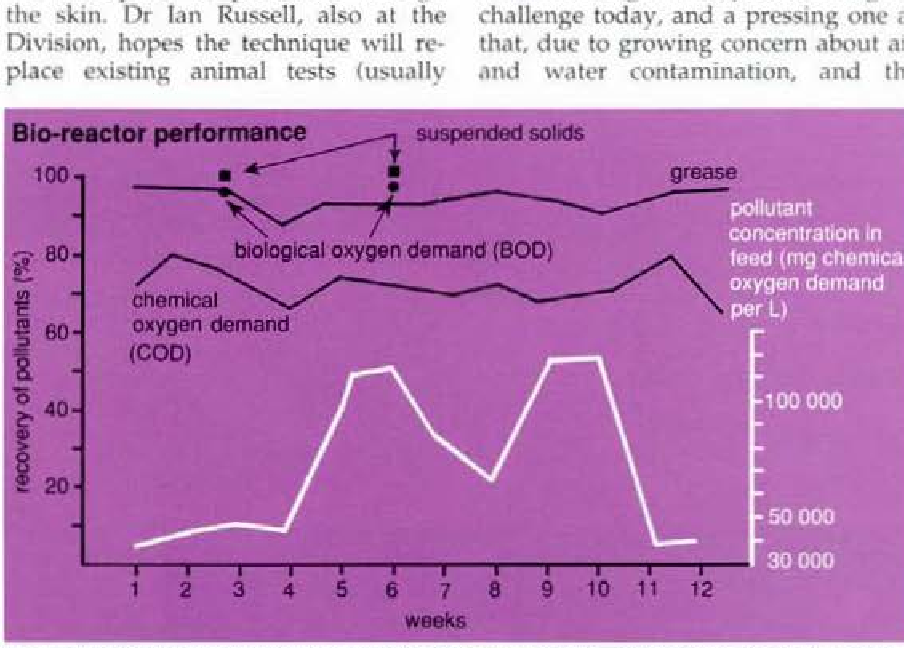
Up to one-quarter of the weight of raw wool is grease, of which about 40% can be recovered for further refinement into industrial lubricants and lanolin for use in toiletries and cosmetics. Unfortunately, due to contamination with agricultural chemicals, refined wool grease contains detectable levels of pesticides currently or formerly in use on sheep, including organophosphates such as diazinon and persistent organochorines such as dieldrin and DDT. (Organochlorine use has ceased as a result of previous CSIRO work and eradication programs by the Australian Wool Corporation and the State Departments of Agriculture.)

At current levels of chemical use, each sheep is sprayed annually with about a gram of organophosphorus pesticide, and about one-fifth of that quantity in pyrethroids, depending on seasonal variations. In total, that represents more than 100 tonnes of active pesticide ingredients on Australia's flocks, although the actual quantity reaching the mills is much lower as most of the chemicals degrade on the sheep during the growing season. Testing of a group of 41 raw wool samples collected in Victoria in 1990 for a range of organophosphorus residues found that, for diazinon, three-quarters of the samples gave readings between 1 and 20 p.p.m.; for other chemicals, most samples recorded levels of less than 1 p.p.m. and none above 20 p.p.m.. (Diazinon produces toxic effects in humans at concentrations above 200 p.p.m.) These figures suggest pesticide concentrations after shearing may be 10 to 100 times lower than those indicated by application rates, but this small survey may not be typical of all farms from year to year.

Nevertheless, while possible health risks from these chemicals appear to be very low, their presence in wool grease affects the image of wool products as being 'pure and natural'. Removal or reduction of the chemical residues present also imposes higher costs for lanolin refiners and retailers here and abroad.

Dr Bill Jones at the Division of Wool Technology has developed a new technique for extracting pesticides from lanolin, which he claims is superior to existing methods used in Europe and the United States. The technique, which can reduce all contaminants to a non-detectable level, is a commercial secret.

In addition, CSIRO is involved in developing a new method for measuring the adsorption of pesticides through the skin. Dr Ian Russell, also at the Division, hopes the technique will replace existing animal tests (usually with rats) that are expensive and of limited value due to differences in permeability between animal and human skin.



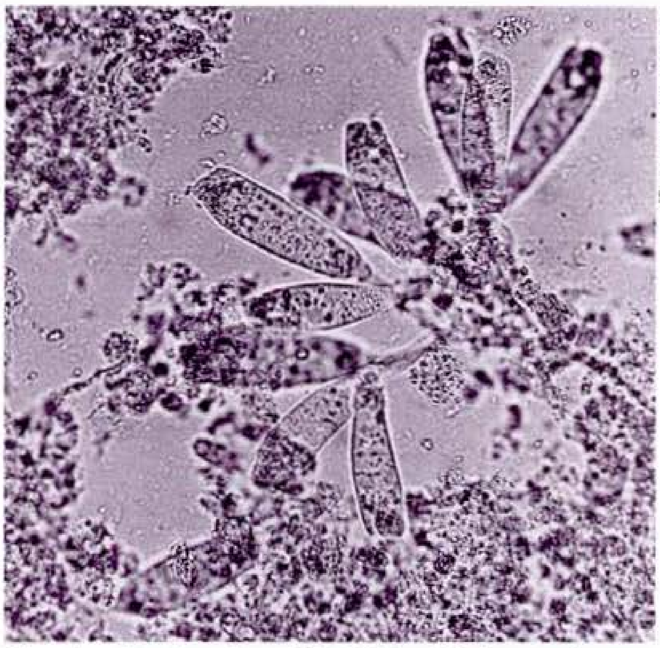
Even with big fluctuations in the concentration of pollutants, a laboratory-sized bio-reactor can remove 70–95% of chemical oxygen demand (COD), suspended solids, grease and biological oxygen demand (BOD) in wool-scouring effluent. (The effluent's BOD reflects the level of organic waste that can be consumed by micro-organisms, while COD is a measure of its oxidisable component.)

The new test — known as an *in vitro* cell diffusion test — uses a mixture of glass, teflon, human skin and calf serum as a model for living human skin and blood. A human trial, conducted in San Francisco, has shown that the test can accurately measure the potential for transfer of chemicals through the skin, thereby offering the basis of a cheap and simple technology for the chemical registration process.

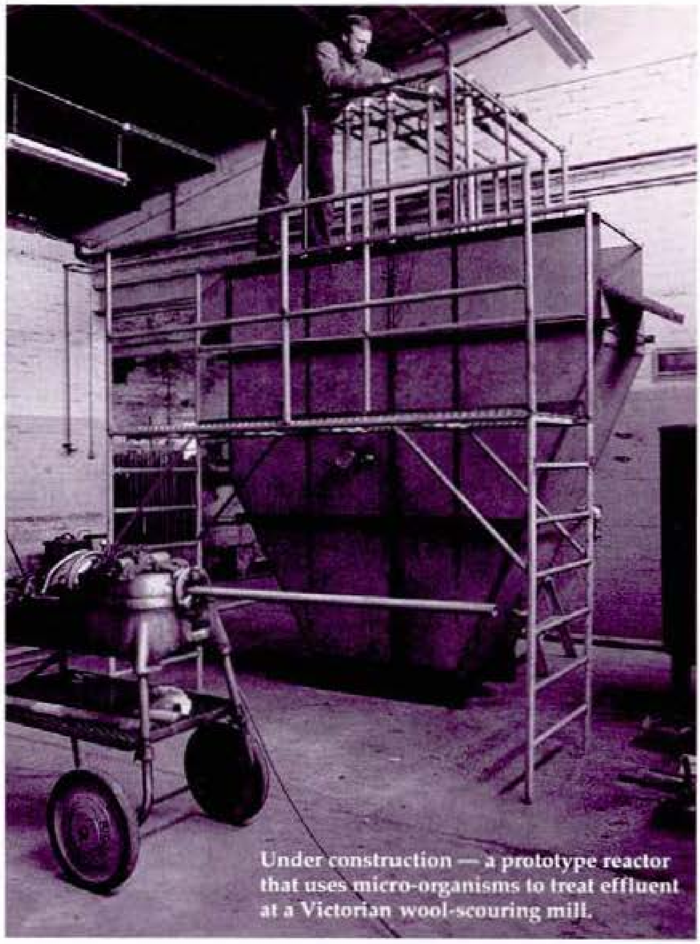
Dr Russell says preliminary results from a study of the chemicals used in sheep treatments indicate that, at current levels, they pose no significant risk to workers and the public due to adsorption through the skin. The wool grease molecules — which do not migrate easily through the skin — appear to retard the adsorption of chemicals by bonding strongly with the pesticide molecules. The early results suggest, he said, that pesticide limits set by the United States Pharmacopoeia for medicinal-grade lanolin — in essence, 3 p.p.m. for total pesticide content and 1 p.p.m. for any one pesticide — are about right to allow safe use with infants.

Australian industry scours about 240 000 tonnes of wool a year. Minimising pollution from wool scouring is a major technological challenge today, and a pressing one at that, due to growing concern about air and water contamination, and the rising cost of disposal of waste, to sewers and landfills, for Australia's 40-odd scouring mills. Solvent scouring mills use large amounts of organic solvents such as hexane and isopropanol that, due to their volatility, are lost to the atmosphere, possibly contributing to photochemical smog. One such mill can lose between 20 and 25 kg of solvent per tonne of wool, or about 300 tonnes of solvent a year.

Aqueous scouring mills have their problems too — not least of which is a



Cigar-shaped protozoa (magnified 200 times) feed on wool grease particles and bacteria.



Under construction — a prototype reactor that uses micro-organisms to treat effluent at a Victorian wool-scouring mill.

steep hike in government charges in the last decade for the discharge of trade waste to sewers. Wool-scour effluent is high in biological oxygen demand (a measure of organic matter) and suspended solids. In Melbourne, the cost of discharging waste containing these two pollutants alone increased more than 85% between 1984 and 1990. Today, a mill in Melbourne with two scouring lines can expect to pay up to $400 000 a year in trade waste charges. Charges in other capital cities are generally higher.

Scouring mills that choose not to pay these charges are generally located in rural areas and treat their waste water on-site to a high standard (known as tertiary treatment) in 'biological lagoons' prior to land irrigation. Other mills partially treat the effluent (called either primary or secondary treatment) to reduce the amount of grease and dirt discharged to the sewer.

Each approach has drawbacks. Scouring effluent is an environmentally damaging and highly stable emulsion of grease, water, detergent, dirt particles, degraded animal protein and soluble salts from sheep sweat. Centrifuges (used in primary treatment) can recover about 40% of the grease and dirt as a spadeable sludge, but most of the pollutants remain in the waste water, making the effluent suitable only for the bigger sewage-treatment works in the cities. Biological treatment (to either a secondary or tertiary standard) usually involves the use of 'digesters' — reactors that use bacteria to break down the organic waste. While effluent treated to this standard can be discharged to a small municipal sewerage system, the capital costs are often high and the waste water is not suitable for direct discharge into the environment.

Tertiary treatment in Australia typically entails the use of a series of large holding ponds — the biological lagoons — in which effluent is slowly degraded by bacteria before disposal by irrigation onto land. Lagooning is considered a highly effective treatment, but many city-based mills do not have adequate land on which to set up a lagoon system. Lagoons can also create odour problems, especially in summer, and tend to produce treated effluent that is high in potassium (more than a gram per litre) and must be applied to soil at a sustainable rate.

Other treatment methods exist — including acid cracking and ultrafiltration — but all methods produce a sludge that can contain unwanted chemicals such as pesticides that may make the material unsuitable for disposal on farmland.

In an effort to eliminate some of the shortcomings of existing treatments, a team of scientists led by Dr Brett Bateup at the Division of Wool Technology has developed a system that combines the efficiency and low cost of biological lagooning with the requirements of a modern city-based mill. Two major limitations with existing methods are the large volume size of digester plants, and the amount of time effluent must spend in biological lagoons before it degrades. Typically, effluent passing through a lagoon system may spend 50 days in a pond containing anaerobic bacteria, followed by 7–10 days in an aerated pond containing aerobic bacteria. It may then require another 20 days in a settling pond.

To accelerate the biodegradation process of lagooning, the researchers found and grew in culture a mixed population of bacteria and protozoa that, under optimum conditions, can reduce the 'residence time' of the effluent from 80 days or more to 48 hours, without loss of treatment quality. The microbial culture comprises eight species of bacteria and a one-celled animal called a ciliate, a protozoan organism that has fine threads or cilia on its surface for movement and feeding.

Previously it had been assumed that ciliates had little role in the breakdown of organic matter, preferring to dine on bacteria and other protozoa. The scientists found, however, that these organisms would also feed on certain organic compounds known as sterols. The bacteria alone were able to break down the fat and wax compounds in the wool grease into free fatty acids and sterols, leaving the ciliates to complete the job and, in doing so, enhance both the rate and extent of wool grease breakdown. The protozoa also substantially reduce the amount of biomass produced, thereby lowering the quantity of sludge created and the cost of sludge disposal per unit of pollutant removed from the effluent.

To reduce reactor volume, the researchers found the best method was to divide the scour effluent into weak and concentrated streams. As much as 70% of the effluent is rinse-water, containing little grease and soluble salts and relatively low levels of dirt and organic matter. By separating out this weak stream, and treating the remaining 30% for only 30 hours instead of 48 hours, they reduced reactor volume by a factor of five.

Trials with a laboratory-sized reactor have produced outstanding results. The system can remove 95 to 98% of grease, biological oxygen demand and suspended solids. The toxic nonylphenol components in detergent waste are degraded by up to 70%, and pesticides such as dieldrin, diazinon, dichlorfenthion and cypermethrin are reduced by between 79 and 92%. The treated effluent produced, Dr Bateup says, would be suitable for discharge into the sewerage system of any small town, while the sludge is potentially a good fertiliser, with high levels of nitrogen and organic carbon.

More recently, the research project has been scaled-up with the construction of a 2000-litre pilot plant (about one-hundredth of full-scale) at a scouring mill in Geelong. The scientists are working on refinements to the process and a further reduction in treatment time to 24 hours.

Brett Wright

More about the topic

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As the wool grows it will acquire a coating of grime.