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# THE TREATMENT AND PURIFICATION OF WOOL AND MOHAIR SCOURING WASTES — A SURVEY

by T. E. MOZES

## 1. INTRODUCTION

Wool and mohair aqueous scouring wastes are known to be of a highly polluting nature. These cannot be discharged into municipal sewers because municipal authorities have been compelled for ecological reasons to demand a high level of purity in these streams. Legislation promulgated over the last couple of years has become ever more stringent in respect of these levels of purity, obviously because of the detrimental effect of pollution on the ecology.

The aim of this survey is to provide a retrospect of the various processes for the treatment and purification of wool and mohair scouring wastes from 1874 to present time, to provide the interested reader with an insight into what has been done in this field and what remains to be done and also into what the

**TABLE 1**  
**SOME PHYSICAL AND CHEMICAL DATA FOR CRUDE WOOL GREASE<sup>1</sup>**

Colour	yellow to pale brown
Density (at 15°C)	0,94 — 0,97
Refractive index (40°C)	1,48
Melting point	35 — 40°C
Free acid content	4 — 10%
Free alcohol content	1 — 3%
Iodine value	15 — 30
Saponification value	95 — 120
Molecular weight	790 — 880
Proportion of fatty acids	50 — 55%
Proportion of alcohols	45 — 50%
Acids: melting point	40 — 45°C
iodine value	10 — 20
mean molecular weight	330
Alcohols: melting point	55 — 65°C
iodine value	40 — 55
mean molecular weight	370

problems are that are associated with this field and also some alternative solutions to these problems. The efficiency and economics of a number of promising processes proposed worldwide are discussed in the last section of this survey. The author trusts that it will contribute towards a better understanding of the pressing problems which wool and mohair scouring wastes present to our society and the solutions which are available at present.

## 2. COMPOSITION OF WASTES

Wastes from the wool and mohair scouring industry are oil-in-water emulsions in which the oily phase consists of relatively fine droplets of wool grease. They contain, in addition to wool grease, dissolved salts (mainly suint), suspended solids and bacteria and are stabilised mainly by a detergent and a suitable builder. The concentrations of the different constituents vary from waste to waste depending on the source of the waste and the chemical additives used during scouring of the raw fibre. The various constituents are discussed below:

### 2.1 Wool Grease

This constituent is often called 'wool wax' and, in its pure state

TABLE 2  
SUMMARY OF THE CONSTITUENTS OF WOOL GREASE<sup>1</sup>

Acidic fraction	Approximate content (%)
<i>n</i> -Acids: 9 members, decanoic to hexacosanoic	7
iso-Acids: 10 members, 8-methylnonanoic to 26-methylheptacosanoic	22
anteiso-Acids 12 members, (+) 6-methyloctanoic acid to (+) 28-methyltriacontanoic	29
-Hydroxy- <i>n</i> -Acids: 4 members, 2-hydroxydodecanoic to 2-hydroxyoctadecanoic	25
-Hydroxy-iso-Acids: 1 member, 2-hydroxy-16-methylheptadecanoic	3
TOTAL	86
Unidentified residue	14

(Table 2 Continued)

Alcoholic fraction	Approximate content (%)
Aliphatics:	
<i>n</i> -Alcohols: 7 members, octadecanol to triacontanol	4
iso-Alcohols: 5 members, 16-methylheptadecanol to 24-methylpentacosanol	6
anteiso-Alcohols: 6 members, (+) 14-methylhexadecanol to (+) 24-methylhexacosanol	7
<i>n</i> -Alkan-1,2-diols: 1 member, hexadecanediol	0,5
iso-Alkan-1,2-diols: 4 members, iso-octadecanediol to iso-tetracosanediol	3
Sterols:	
5 members, cholesterol	20
7-oxocholesterol	5
cholestane-3,5,5-triol	2
cholesta-7-en-3-ol	} 2
cholesta-3,5-dien-7-one	
Isocholesterol:	
6 members, anosterol	10
dihydrolanosterol	10
agnosterol	1
dihydroagnosterol	4
7,11-dioxolanost-8-en-3-ol	} 2
7-oxolanost-8-en-3-ol	
Hydrocarbons:	
Number unknown, structure unknown	1
TQTAL	78
Unidentified residue	22

('anhydrous lanoline') it can be described as a pale yellow substance of melting point 35 to 40°C; insoluble in water, sparingly soluble in alcohol and freely soluble in ether and chloroform. Truter<sup>1</sup> published some physical and chemical data relating to crude wool grease as given in Table 1.

Essentially wool grease is a complex mixture of high molecular weight esters, which also contains small percentages of free acids, alcohols and hydrocarbons. Little seems to be known of the specific chemical compositions of the esters. According to the same author<sup>1</sup>, wool grease alcohols fall into three classes: aliphatic, sterols and isocholesterols. The acids include the normal

series as well as iso, ante-iso and hydroxy types. A summary of the constituents of wool grease, as published by Truter<sup>1</sup>, is given in Table 2.

Some additional research work, particularly in the field related to composition of wool grease acids, was carried out by Downing<sup>2</sup>, Truter<sup>3</sup>, Pelick<sup>4</sup> and Fawaz<sup>5,6</sup>. Their findings have been published by Motiuk<sup>7</sup>, as summarised in Table 3. Detailed information on the composition and properties of wool grease, published during the last century, can be found elsewhere<sup>8-37</sup>.

## 2.2 Dissolved Salts

The dissolved salts present in scouring wastes originate from two sources:

- (1) the suint fraction present on the raw wool or mohair fibre, and
- (2) soluble chemical additives added during scouring (mainly sodium carbonate in alkaline scouring).

Suint is the water soluble constituent of the fleece and consists largely of potassium and sodium salts of fatty acids and peptides together with urea and colouring materials. The main inorganic component is potassium comprising 60% of the calcined suint residue (see Table 4). The organic acid fraction includes formic, acetic, propionic, butyric, valeric, oxalic, succinic, glutaric, malic, glycollic, citric acid and others. Some of the organic compounds isolated in suint are given in Table 5. Additional information on the composition of suint can be found in the literature<sup>38-45</sup>.

**TABLE 3**  
**SUMMARY OF THE AVERAGE COMPOSITION OF WOOL GREASE ACIDS (1960—1974)<sup>7</sup>**

Acids	Chain length	% of Wool Grease Acids
Normal acids	C <sub>8</sub> - C <sub>38</sub>	10
Iso acids	C <sub>8</sub> - C <sub>40</sub>	22
Anteiso acids	C <sub>7</sub> - C <sub>41</sub>	28
Normal $\alpha$ -hydroxy acids	C <sub>10</sub> -C <sub>32</sub>	17
Iso- $\alpha$ -hydroxy acids	C <sub>12</sub> -C <sub>34</sub>	9
Anteiso $\alpha$ -hydroxy acids	C <sub>11</sub> -C <sub>33</sub>	3
Normal $\omega$ -hydroxy acids	C <sub>22</sub> -C <sub>36</sub>	3
Iso $\omega$ -hydroxy acids	C <sub>22</sub> -C <sub>36</sub>	0,5
Anteiso $\omega$ -hydroxy acids	C <sub>33</sub> -C <sub>35</sub>	1
Polyhydroxy acids		4,5
Unsaturated acids		2
<b>Total</b>		<b>100%</b>

**TABLE 4**  
**ANALYSIS OF SUINT-ASH<sup>1</sup>**

Potassium	60%	Carbonate	26%
Sodium	2%	Chloride	4%
Calcium	1%	Phosphate	1%
Magnesium (as oxide)	1%	Sulphate	3%
Iron oxide	trace	Silicate	1%

### 2.3 Suspended Solids

The fraction of suspended dirt of inorganic nature (hereafter called 'suspended solids') in the scouring wastes includes predominantly sand and dust particles originally on the fibre. These clay particles, varying within a wide range of sizes, have been found to be associated to a certain extent with wool grease<sup>46-48</sup>. The particle size distribution of wool and mohair scouring wastes<sup>49,50</sup> has been found to follow a bell-shaped distribution in the 0.1 to 400  $\mu\text{m}$  range, with a large portion of the suspended solids varying in size between 0.1 to 50  $\mu\text{m}$ . Vegetable matter originating from the pasture fields and fibre originating from the scoured wool and mohair are also present in the various liquid wastes. Detailed information about vegetable matter composition is available in the literature<sup>51,52</sup>.

### 2.4 Detergent

In modern scouring practices mostly synthetic non-ionic detergents are used. Chemically they have a hydrophilic 'head' and a hydrophobic 'tail'. The hydrophobic tail adsorbs on the surface of the grease droplet, stabilisation of the emulsion occurring by means of the hydrophilic head. A wide range of non-ionic detergents is available on the market<sup>53-59</sup>.

### 2.5 Bacteria

It is of common knowledge that wool scouring wastes tend to putrefy following excessive storage at ambient temperature and this phenomenon is probably associated with the presence of bacteria. The mechanism involved is believed to be extremely complex due to the complex nature of the other contaminants and at present does not seem to be fully understood. It is possible, however, that bacterial activity is somehow connected with the oxidation of wool grease<sup>60</sup> and, therefore, with emulsion stability<sup>61</sup>.

Measurements of bacterial activity on wool scouring wastes have been carried out in the past<sup>61</sup>, indicating that levels of bacteria of the order of 100 000 colonies/ml are fairly typical in fresh wool scouring liquors. These levels can increase by one or two orders of magnitude in fresh liquid sludges obtained from wool scouring mills.

TABLE 5

SOME OF THE ORGANIC COMPOUNDS ISOLATED IN SUINT<sup>1</sup>

Steam-volatile components		Percentage	Other aliphatic compounds
Formic acid	H COOH	trace	Oleic acid Stearic acid
Acetic acid	CH <sub>3</sub> COOH	60	
Propionic acid	C <sub>2</sub> H <sub>5</sub> COOH	25	
Butyric acid	C <sub>3</sub> H <sub>7</sub> COOH	5	
Valeric acid	C <sub>4</sub> H <sub>9</sub> COOH	4	
Caproic acid	C <sub>5</sub> H <sub>11</sub> COOH	3	
Oenanthalic acid	C <sub>8</sub> H <sub>13</sub> COOH	trace	
Caprylic acid	C <sub>7</sub> H <sub>15</sub> COOH	trace	
Benzoic acid	C <sub>6</sub> H <sub>5</sub> COOH	3	
Phenol (derived from a phenyl sulphonic acid)	C <sub>6</sub> H <sub>5</sub> OH	trace	
Other compounds			
Oxalic acid	HOOC COOH	Not supplied	Ammonia Monomethyl-amine Trimethylamine
Succinic acid	HOOC CH <sub>2</sub> CH <sub>2</sub> COOH		
Glycollic acid	CH <sub>2</sub> (OH) COOH		
Lactic acid	CH <sub>3</sub> CH(OH) COOH		
Malic acid	HOOC CH <sub>2</sub> CH(OH) COOH		
Glycine	CH <sub>2</sub> (NH <sub>2</sub> ) COOH		
Leucine	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(NH <sub>2</sub> ) COOH		
Tyrosine	HO Ph CH <sub>2</sub> CH(NH <sub>2</sub> ) COOH		
Uric Acid	C <sub>5</sub> H <sub>4</sub> O <sub>3</sub> N <sub>4</sub>		

### 3. TREATMENT AND PURIFICATION OF WASTES

The first attempts to treat and purify wastes from the wool and mohair scouring industry date back to the previous century. The ecological damage caused by the polluting nature of these wastes was already well known in those days and the recovery of lanoline for commercial uses was attempted, although on a relatively small scale.

The remainder of this section is devoted to a chronological summary of the development of the different treatment methods during the last century up to the stage that they are known today.

#### 3.1 Centrifugal Separation

The history of the centrifugal separation of wool grease from scouring liquors is also the history of the design of a special centrifuge. As early as 1884 attempts were being made in Germany to separate wool grease centrifugally, using cream separators. These attempts failed because of the fine mud which

invariably clogged the machines. Consequently, frequent stoppages for cleaning were inevitable<sup>1</sup>.

Smith and Leach<sup>62</sup> attempted to solve the problem by reducing the bulk of liquor to be centrifuged. The liquors were evaporated down to one-tenth of their initial volume in a multiple-stage vacuum still, and then centrifuged. It was intended that the aqueous phase containing potassium salts from the suint and sodium salts from the soap, would be evaporated to dryness and calcined to give potassium and sodium carbonates, and at the same time, the wool grease would also be recovered. In practice, however, the grease was of poor quality and still contained a large amount of dirt. Potassium recovery failed completely because, as we now know, the centrifuges could not remove all the grease from the emulsion and the subsequent calcining of the aqueous liquors gave rise to a black, sticky mass<sup>1</sup>.

As the years went by the design of centrifuges continued to improve. In the last few decades, two types of centrifuges have been used for the separation of wool grease and suspended solids from conventional wool scouring liquors, namely centrifugal clarifiers and separators. The former are used for desludging wool scouring liquors and produce only a sludge phase and a liquid phase. The latter is then separated into a cream phase rich in grease, a sludge phase rich in both grease and suspended solids and a middle, or effluent, phase.

A typical centrifugal clarifier operates on the principle of flow of feed liquor through the narrow spaces formed by a set of conical discs. The solids collect on the top wall of each space and slide down into the sludge space. The clarified liquor is discharged from the bowl under pressure by means of a centrifetal pump.

A typical bowl speed for this type of centrifuge is 6 500 rev/min and a typical value for centrifugal force, 8 000 G (equivalent to a centrifugal acceleration of 78 400 m/s<sup>2</sup>). Additional information relating to the operation of centrifugal clarifiers is available elsewhere<sup>63</sup>.

A typical centrifugal separator operates on the principle of centrifugal acceleration and radial distribution of the feed liquor by means of a suitable distributor, flow through the rising channels formed by a set of conical discs and further distribution into the narrow disc interspaces, the whole unit constituting a separation chamber.

The separated heavy-phase liquid (effluent) is discharged from the bowl via the outer ring weir and the light-phase liquid (cream) via the inner weir. Solid matter is deposited in the sludge chamber<sup>64</sup>. A separator bowl may be converted into a clarifier bowl by blocking the rising channels and the heavy-phase outlet.

A typical bowl speed for this type of centrifuge is 8 500 rev/min and a typical value for centrifugal force, 10 000 G (equivalent to a centrifugal acceleration of 98 000 m/s<sup>2</sup>). Additional information about the operation and main-



tenance of centrifugal separators can be found elsewhere<sup>65</sup>. The operation of a centrifugal separator is illustrated in Fig. 1.

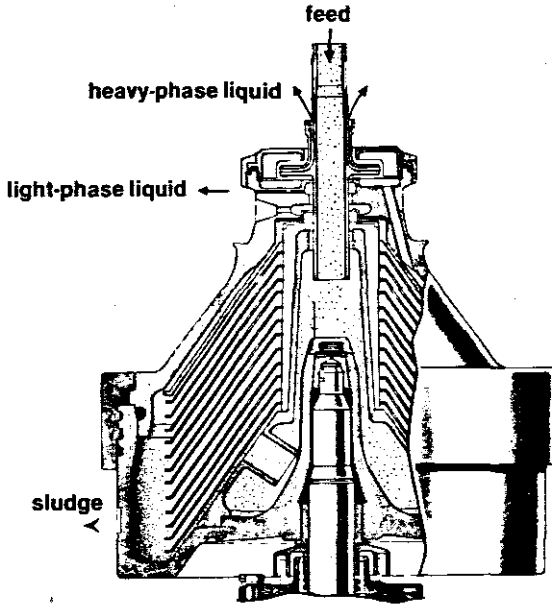


FIGURE 1

Schematic representation of a typical industrial centrifugal separator<sup>64</sup>

The efficiency of the centrifugal process as far as wool scouring liquors is concerned, has been extensively investigated. In one such investigation<sup>66</sup>, a sludge discharge centrifuge (also called 'primary centrifuge') was used to determine the effects of different parameters on the recovery of grease.

The percentage recovery was found to be independent of temperature in the range of 57 to 82°C and of feed flow-rate in the range of 4 500 to 6 300 ℓ/hr but was inversely proportional to the gravity disc diameter. (The latter device is used for adjusting the phase separation in the centrifuge.) In general, the machine was inefficient at settings that gave very low or very high concentrations of grease in the product, the optimum concentration being 10 to 20%.

Various studies into the efficiency of grease recovery from wool scouring liquors by primary centrifugal separation<sup>66-74</sup> have shown that theoretical values of 50 to 70% and practical values of 40 to 60% may be expected, although the efficiency can drastically decrease, in some cases, to values as low as 25% for liquors originating from wools with high levels of oxidised grease<sup>75</sup>.

The efficiency also depends, *inter alia*, on the initial concentration of the liquor from the scouring bowls. It is customary to allow this to reach 2 to 2.5% grease, when it would be considered that a 35% recovery would be poor and a 50% recovery would be usual. If the original grease content rises to, say 4%, then recoveries as high as 75% are not too difficult to obtain. Moreover, there appears to be some evidence that liquors containing nonionic detergent give a higher recovery than those containing soap<sup>63</sup>.

Investigations into the mechanism of wool grease fractionation during centrifuging<sup>76-79</sup> have proved that grease recovered in the cream obtained by centrifuging of scouring liquors (or 'influents') can be associated with the unoxidised or non-polar grease fraction while that remaining in the effluent phase from centrifuging, associated with the oxidised or polar grease fraction. One of the reasons for this fraction not being separated centrifugally is probably its small difference in density compared with that of the aqueous phase and its association with the dirt.

The cream phase from primary centrifuging is usually further concentrated in grease by means of a secondary or a secondary and a tertiary centrifuge in series. Typical grease concentrations delivered by these centrifuges are reported<sup>80</sup> to be about 70 and 99% for the former and the latter, respectively. Important parameters which affect grease recovery are reported to be feed concentration, flow rate and temperature, as well as the diameter of the gravity disc<sup>80</sup>.

The effect of various parameters on grease recovery during the centrifugal process has been studied extensively. Amongst others, the effect of diameter of the gravity disc<sup>66,81-83</sup>, diameter of sludge discharge outlet<sup>66,83</sup>, feed liquor flow rate<sup>66,80,83</sup>, settling time of feed liquor before centrifuging<sup>66,72,84</sup>, suint and detergent concentration in feed liquor<sup>81,84</sup> and temperature and pH of feed liquor<sup>72,81,84</sup> has been reported in the literature. Other factors worth mentioning, and which have been investigated, are the effect of suspended solids concentration<sup>77,85</sup>, type of detergent present in feed liquor, its concentration and its influence on grease droplet size distribution<sup>77,86,87</sup>, the effect of storage before centrifuging<sup>77</sup> and the effect of increase in centrifugal efficiency on the quality of the cream<sup>88</sup>.

More recent studies on the technique of centrifuging<sup>89</sup> have shown that this operation helps to maintain the efficiency of a scouring liquor during a continuous wool scouring operation allowing, at the same time, profitable grease recovery. Various experimental procedures have been devised and published for the estimation of grease recovery from wool scouring liquors<sup>90,91</sup>.

Two industrial processes for the treatment of wool scouring liquors and grease recovery have been developed during the last decade. These processes are the Garap system and the ITF/Alfa Laval system.

The Garap system (Fig. 2) comprises a filter and a range of Garap disc centrifuges for continuous treatment of the first bowl scouring liquor and

recovery of wool grease from it<sup>92-94</sup>. It has been claimed<sup>94</sup> that savings in heat, water usage and detergent can be achieved using this system. It has also been reported<sup>93,94</sup> that the grease recovery level and the quality of the wool grease have both been improved with the implementation of this technique. The process is being used at industrial level in various wool scouring mills in Western Europe. One of these mills has further developed the process by combining the Garap centrifugal system with a large evaporation plant<sup>95</sup>, thus creating the so-called 'Dewavrin' process.

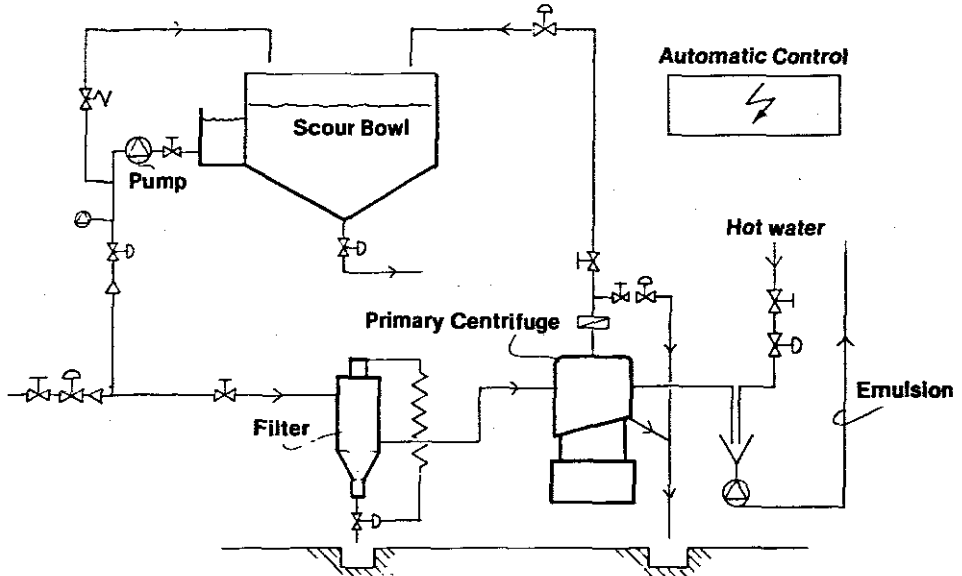


FIGURE 2  
Flow diagram of the Garap process<sup>94</sup>

The ITF/Alfa Laval system, shown in Fig. 3, comprises a range of centrifugal clarifiers, concentrators and purifiers, a horizontal decanter centrifuge (see below) and an evaporator, to yield an in-house treatment of the waste liquors from all five scouring bowls<sup>95,96</sup>. The main degreased effluent stream, originating from the centrifugal separators is fed into a 4-effect evaporator of the falling film type<sup>95</sup>. The concentrate from the evaporator passes to a sedimentation tank and it is finally combined with the solid sludge originating from the decanter centrifuge. The condensed water from the evaporator is recycled and re-used in the scouring plant, the process thus constituting a system of zero discharge<sup>95</sup> (no liquid effluent). First and second grade wool grease and solid sludge are obtained as by-products of this process<sup>96</sup>. Grease recovery levels are reported<sup>96</sup> to be good (of the order of 75%).

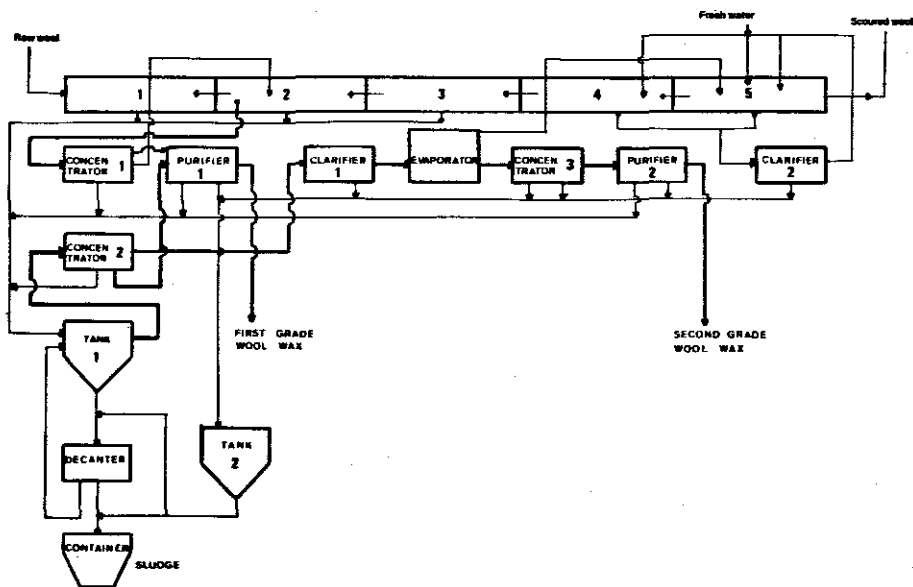


FIGURE 3  
Flow diagram of the ITF/Alfa Laval process<sup>96</sup>

Over the last decade a new type of centrifugal separator, the horizontal decanter centrifuge, has been introduced into the market for the treatment of wastewater in general and of wool and mohair scouring wastes in particular. In general, horizontal decanter centrifuges are capable of dealing with wastes with much higher suspended solids content than those which disc centrifuges are capable of dealing with. They differ from the latter in their design as well as in their operating conditions. Typical figures for centrifugal speed vary from 800 to 2 500 rev/min, those for centrifugal force, from 300 to 3 300 G (equivalent to a centrifugal acceleration of 2 900 to 32 300 m/s<sup>2</sup>) and those for residence time during centrifuging, from 2 to 6 min (in contrast with the disc centrifuge for which a figure of 1 min would be considered as typical). Horizontal decanter centrifuges are normally used in conjunction with some destabilising pre-treatment technique and will be elucidated further in the respective section.

Decanter centrifuges can be basically of two types, i.e. co-current and counter-current<sup>64,97</sup>. The centrifugal drum of the first type of decanter centrifuge is horizontal and comprises two sections, i.e. a cylindrical section for *clarification* purposes and a conical section for *dewatering* purposes. The drum and the internal screw rotate in the same direction but at a different circumferential speed, both of which can be pre-selected. Centrifugal force

separates the heavy particles of solid material which settle on the walls of the drum. The clarified liquid or centrate flows out of the apertures of the overflow weir. The sedimented solids (solid sludge) are discharged by the screw through the respective discharge aperture. Both *sludge* and *centrate* flow concurrently, thus avoiding the turbulence prevailing to some extent in the counter-current centrifuges of this kind and, to a large extent, in the disc centrifuges. The operation of a horizontal decanter centrifuge of the co-current type is illustrated in Fig. 4.

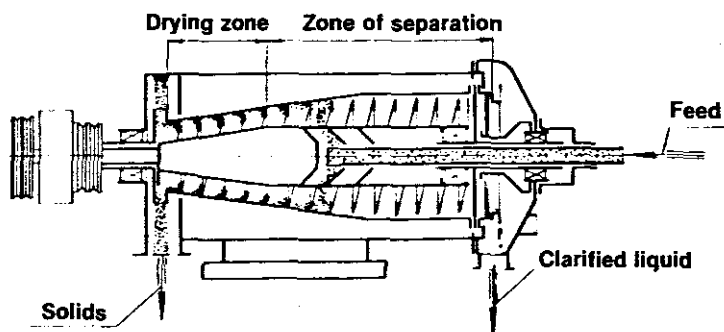


FIGURE 4

Schematic representation of a horizontal decanter centrifuge of the co-current type<sup>64</sup>

### 3.2 Flotation

Flotation is a gravity separation technique in which gas bubbles are used to float solid particles by reducing their relative density. The bubbles become attached to the surface area of these solid particles forming agglomerates, whose lower density makes them rise to the surface to form a froth which can then be collected.

Until the early 1970's the gas bubbles were generated by a method called 'dispersed air flotation'. Usually this was achieved by means of a high speed agitator in combination with an air sparger. Two other methods were then investigated and subsequently applied to the treatment of wool scouring wastes, i.e. dissolved air flotation and electroflotation. In the former, air is dissolved in the liquid under pressure and then precipitated at atmospheric pressure while in the latter, low voltage DC current is used to generate hydrogen and oxygen bubbles by means of two inert electrodes.

Wool grease emulsions form very stable foams when they are aerated. Battage was one of the earliest methods of removing grease from scouring wastes which made use of the stability of the froth. The liquid was beaten by hand paddles or bats and the resultant foam was skimmed off and melted down. The efficiency of the operation was extremely low, although it has been stated that recoveries of up to 25% could be obtained<sup>1</sup>. A modern version of

the battage process was developed by Mertens<sup>1,98</sup>. He replaced the hand paddles by electrically driven ones and scaled up the operation. The froth produced by beating cold wastes overflowed the flotation cell, was then sprayed with water and allowed to stand for separation of the phases to take place and it was finally skimmed off. The foam was broken by heating at 130°C in an autoclave under pressure conditions of 200 to 300 kPa. An acceptable figure for the residual grease content in the liquors treated by this method would be around 0,5%<sup>1</sup>.

In 1914, Barber<sup>99</sup> began the development of what is now known as the 'jet process'. Firstly, the scouring liquors were allowed to stand so that the coarse dirt could settle out. The liquid then passed into a trough, at the bottom of which were a number of fine jets through which compressed air could be blown. Above each jet there was a tubular chamber fitted with perforated baffle-plates. The force of the jet carried the foam out of this chamber and through a sloping, perforated cover-plate. The foam was collected in a 'collecting' tank while the liquid ran back to the flotation tank through a draining trough<sup>1</sup>. The system was later re-designed and improved by Burgard<sup>100</sup>. The foam, after being washed with water sprays and re-dispersed by heating with boiling water, was pumped into an automatic autoclave working at 120 to 130°C and under 240 kPa pressure, from which grease and water were withdrawn separately<sup>101</sup>. The efficiency of the Barber jet process had an effective upper limit of about 50%, and it had to be operated on liquors having a fairly high grease content, i.e. about 2% or more<sup>1</sup>.

In the early 1950's Evans and Ewers<sup>102</sup> devised a process, called the CSIRO aeration process, which was subsequently used commercially in Australia<sup>103</sup>. Froth flotation of scouring wastes was produced by rotation of an impeller which caused air to be drawn through its internal tube and, being dispersed throughout the liquid, the resultant froth overflowed the flotation chamber and was re-dispersed in the liquid. After 15 min the impeller was stopped, the foam allowed to accumulate and collected. It was found, however, that at residual grease contents in the liquor of 0,3 to 0,8% no more wool grease could be recovered. The grease concentration of the froth could be increased from about 10 to 50% by gentle stirring at 60°C. Further concentration was achieved by autoclaving at 115°C<sup>98,99</sup> which resulted in the separation of grease from the two other phases (water and a mixture of grease, dirt and water).

The effect of pH and temperature<sup>102</sup>, grease, suspended solids and detergent content of feed liquor<sup>102</sup>, storage of feed liquor prior to treatment<sup>103</sup>, aeration time<sup>102,103</sup>, addition of foam stabilisers<sup>1</sup> and addition of flocculants<sup>104-109</sup> on flotation efficiency was investigated by several workers in this field.

A commercial plant similar to that of the CSIRO aeration process was then commissioned. The scouring liquors were passed through a coarse filter

and then settled in a large sedimentation tank. The pre-heated liquors were cooled to below 30°C, floated in two flotation tanks in series (residence time 10 min each) and washed in two washing tanks in series. The final concentrate was dispersed in 1% sodium carbonate by gentle agitation at 85°C. The overall yield from an average scouring train was found to be about 40%, irrespective of whether soap or synthetic anionic detergent was used for scouring.

Addition of various chemicals concomitantly with flotation was also studied<sup>104-109</sup>. Pilot scale studies<sup>108</sup> on flotation of soap scouring wastes by means of a mixture of air and carbon dioxide (the latter was required to reduce the pH of the feed to 8) in conjunction with a 1.5% (m/v) addition of calcium chloride resulted in reductions of suspended solids, grease and BOD of 97, 96 and 85%, respectively. Other studies<sup>105-107,109</sup> involving injection of a mixture of air and gaseous chlorine (1.5 to 5 ppm on scouring waste volume basis) to the flotation cell showed an eightfold increase in grease enrichment of the concentrate as compared with that obtained by normal flotation standards.

Over the past few years the flotation technique has been revitalised in the form of two improved techniques, i.e. electroflotation and dissolved air flotation. As mentioned elsewhere, improvements in this field were mainly related to the generation of air bubbles of smaller size than those present in normal flotation operations. A reduction in bubble size resulted in an increase in surface area available for flotation. This ultimately led to an increase in grease recovery in the concentrate and to an improved purification of the clarified liquors.

The electroflotation technique has been studied recently by several workers<sup>110-112</sup>. Passage of direct current through two inert electrodes produces hydrogen and oxygen bubbles, with size distribution reported by some workers<sup>113</sup> to be in the range of 10 to 60  $\mu\text{m}$  and by others<sup>60</sup>, in the range of 100 to 200  $\mu\text{m}$ . Modern electrode materials in use are mild or stainless steel for cathodes and graphite stainless steel, platinised titanium or lead dioxide coated in titanium for anodes. Simple flotation cell designs with the electrodes at the bottom are generally used. The operation of a typical electroflotation system is illustrated in Fig. 5.

Application of this technique to wool scouring wastes has been reported<sup>113,114</sup>. In the first of these investigations<sup>114</sup>, good grease removals were reported using steel cathodes and lead dioxide coated anodes. Parameters investigated were pH range, coagulant type and dosage, retention time, current density and temperature. For satisfactory performance, the pH had to be reduced from 10 to 7. Aluminium chlorohydrate and ferric chloride were found to be effective coagulants. The optimum current density was 30 amp/m at a voltage of 6 volts. A retention time of 1 hour reduced the grease level of the feed by 97.5%.

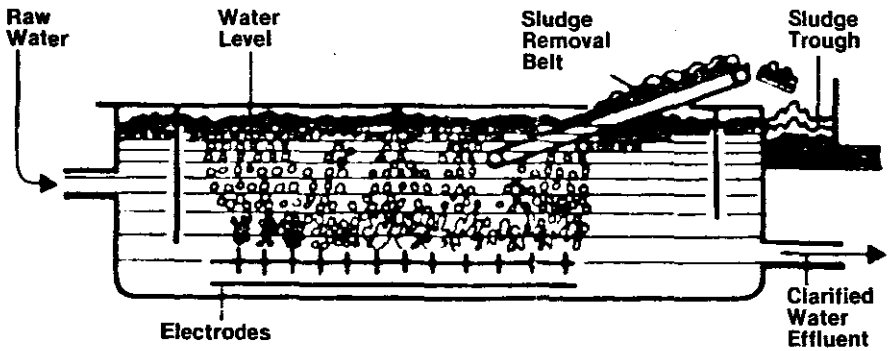


FIGURE 5

Schematic representation of an industrial electroflotation cell<sup>113</sup>

In a more recent study<sup>113</sup>, a reduction of only 72% in the grease level of the feed was obtained with inert electrodes. Electroflotation using aluminium sacrificial anodes (electrocoagulation), however, showed that if the feed was partially degreased by dispersed air flotation prior to electroflotation, the above reduction could be increased to render residual liquors with a grease content lower than 0,05%.

A dissolved air flotation system consists essentially of a flotation cell and a saturator. Air bubble size for industrial flotation systems of this kind has been reported by some workers<sup>113</sup> to be close to 80  $\mu\text{m}$  and by others<sup>60</sup>, in the range of 30 to 120  $\mu\text{m}$ . The operation of a typical dissolved air flotation system is illustrated in Fig. 6.

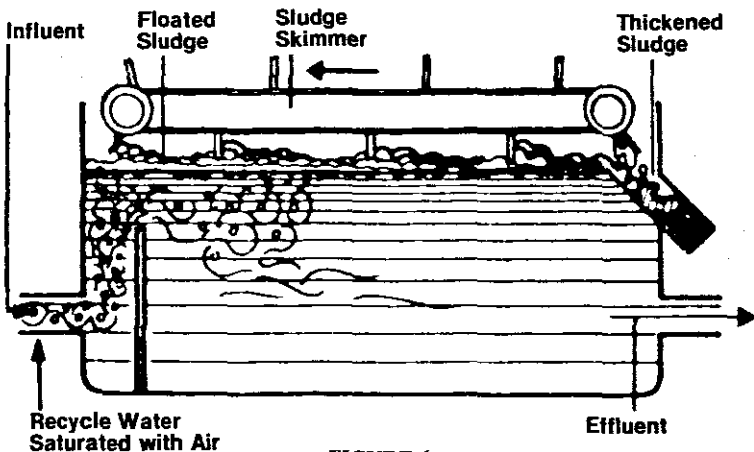


FIGURE 6

Schematic representation of an industrial dissolved air flotation cell<sup>113</sup>



An investigation relating to the use of this technique on wool scouring wastes<sup>115</sup> showed that reductions in the grease and suspended solids levels of the feed of 97 and 99%, respectively, could be obtained. However, other workers<sup>116</sup> found that the use of dissolved air flotation in conjunction with polyelectrolyte addition gave lower reductions (up to 40% for grease and 50 to 80% for suspended solids). It was reported in a more recent study<sup>113</sup> that ageing of wastes before flotation could adversely affect the reduction in grease level.

### 3.3 Acid Cracking

This technique was widely used during the first half of the century. In the early 1950's, however, soap was replaced by synthetic detergent in normal scouring practices and the use of this technique subsequently declined, although it is still being used in a few isolated cases.

In a traditional acid cracking plant, soap scouring wastes are passed through a coarse filter to remove fibres and large pieces of vegetable matter, before being run into the cracking tanks. Enough sulphuric acid is added to reduce the pH to 4 and the mixture is well agitated by means of compressed air or by paddles fitted to a tank. Thorough cracking of the soaps is essential if problems in the filter presses are to be avoided. Sometimes a small percentage, up to 20%, of the sulphuric acid can be saved by using calcium salts as cracking assistants. After the acid has been added, the liquor is allowed to stand for a few hours so that the grease can settle. A small amount of grease floats to the surface and forms a scum. The supernatant liquid is then drawn off from under a scum barrier and run to waste, and the greasy sludge or 'magma', still containing 90% water, is pumped to hot-storage tanks from which it is fed continuously to steam-heated filter presses. Limiting conditions in the presses are 400 kPa maximum pressure and 80°C minimum temperature. Water and wool grease pass through the filter and are collected in a vessel which separates the hot grease by allowing it to overflow into storage tanks. The residue in the filter press is known as 'sud-cake', and can contain up to 20% grease which cannot be economically pressed. It also contains about 3% nitrogen and is used for the preparation of fertilizers. If the treatment in the cracking tank has been thorough, the sud-cake is hard and is easily removed from the press. If, however, the cracking has been incomplete and soaps have reached the press, the sud-cake is soft and sticky and the filter cloths soon become blocked.

A modified acid cracking process concerning the 'magma' filtering stage was introduced in Germany<sup>88</sup>. The temperature was not raised above 60°C and the pressure was not allowed to exceed 340 kPa. Under these relatively mild conditions, only water was discharged during pressing. Batches of filter cake containing 50 to 60% water were then transferred to steam-jacketed extraction vessels. Light petroleum (b.p. 80 to 110°C) was added, the temperature raised to 70°C and the mixture thoroughly stirred or churned for about 5 min and

then allowed to stand. After 15 min most of the insoluble matter had settled, and the supernatant petroleum solution could be drawn off. The extraction was repeated four to six times, depending upon the grease content of the filter cake. Petroleum fractions heavy in grease, i.e. containing 8 to 20%, were sent forward for distillation while others were used again for the extraction of further batches of filter cake. The main disadvantage of this process was the large amount of solvent required, usually 25 to 30 parts for each part of grease extracted, and the consequent high steam consumption in distillation. In general, about 15% grease remained in the residue after extraction despite the use of large volumes of solvent. If higher boiling petroleum fractions were used, the extraction was more efficient, but this gain had to be balanced against the darker colour of the extract and the possible need for subsequent bleaching. After the extraction, the residue was blown with live steam to strip all the solvent, and the resulting slurry was pressed to remove water. Finally, the residue was transferred to a steam-jacketed vacuum drier where the final water content was reduced to 3%. The product was then regarded as suitable for use in fertilizer blends.

In general, the maximum efficiency of grease removal has been found not to exceed 70%<sup>1</sup> for all kinds of acid cracking processes. There were two main reasons for the loss of grease in the recovery process. Firstly, the emulsion was never entirely broken. As much as 10% of the grease originally present could remain in the supernatant liquid which was discharged after precipitation of the magma. Secondly, about 20% of the grease remained in the sud-cake.

An investigation into acid cracking of wool scouring wastes by ion-exchange resins was patented<sup>117</sup> in 1950. It was based on the principle of replacement of sodium cations by protons. Wool-scouring wastes were passed through a bed of ion-exchange resin until the effluent became cloudy. The wool grease and dirt deposited on the resin were extracted with a suitable solvent, e.g. chloroform or ethyl acetate, and the cleaned resin was regenerated by washing with acid. The complete cycle could then be repeated. As far as is known, this process was not used on a large scale.

From 1950 to date, the traditional method of 'acid-cracking' wool scouring wastes has suffered with the advent of nonionic detergents although it has been claimed<sup>118,119</sup> that tannins or bentonite could be used to destabilise the colloidal protection offered by these detergents in acidified wastes. In general, where nonionic detergents were used in the emulsification of grease, incomplete flocculation was usually observed and this at higher dosage rates than required for ionic detergents<sup>120</sup>.

During the past 30 years, the use of the acid cracking technique in different countries has been widely reported. In the USA, for instance, traditional acid cracking to a pH of 3.5 was used<sup>73</sup>, but the technique was virtually abandoned since the advent of synthetic nonionic detergents in normal scouring practice. However, in 1955, an acid cracking process by means of

sulphuric and tannic acids was suggested in a patent<sup>121</sup>. Wool scouring wastes were acidified to a pH of 3,2, tannic acid was added (0,02% v/v) and the heated wastes were stirred and allowed to stand for 15 min before phase separation. Lanoline recovery from the combined sludge phase was carried out successfully.

In Japan, the acid cracking technique was very popular before the Second World War and it constituted an important source for lanoline. However, most of the installations were destroyed during the war and in the post-war years no serious efforts were made for their reconstruction, mainly due to the advent of nonionic detergents. New developments in the field were then patented<sup>122</sup>. Treating wool scouring wastes with sulphuric acid to a pH of 3 to 4, separating the combined sludge phase from the aqueous phase and extracting it with a water immiscible solvent for grease recovery and with a water miscible solvent for recovery of soapy products was suggested. Good purification of wastes and phase separation were reported<sup>122</sup>.

In Czechoslovakia, the acid cracking process, which has been seldom used in the last two decades, consisted traditionally of a pre-settling stage, an acid cracking stage (to a pH of 3 to 3,5) and a settling stage (for a few hours) for phase separation<sup>74,84</sup>. The upper phase combined with the bottom phase (combined sludge phase), containing suspended solids and grease, was heated to 95°C and filtered in a pressure filter previously heated to the same temperature. The filter cake obtained by this process had a grease level of about 15% and could be used as a low grade fertilizer. The aqueous middle phase obtained after acid cracking could be disposed of in the drain after suitable neutralisation with alkali.

In the United Kingdom, acid cracking was widely used in the past and is still being used in several places nowadays, mainly with the aim of purifying wool scouring wastes. The process involved similar stages as those of the process used in Czechoslovakia<sup>71</sup>. Heating of the combined sludge phase prior to pressure filtration was done by means of live steam, the resultant aqueous stream being recycled to the phase separation tank. Studies into various aspects of the acid cracking process<sup>72</sup> revealed that the main factors which caused an increase in the free fatty acids content of recovered lanoline were heat, moisture and presence of mineral acids. The increase in free fatty acids content was found to adversely affect the quality of the recovered lanoline. It was also reported that the filter cake obtained from this process contained 15 to 25% grease and reasonably high levels of nitrogen and could, therefore, be used as a fertilizer<sup>123,124</sup>.

In New Zealand the acid cracking process was widely used for soap scouring wastes and practically abandoned since the advent of non-ionic detergents into scouring practices, mainly due to the poor phase separation obtained in the latter case.

Funke carried out a comprehensive study on waste treatment<sup>119</sup> and

reported that the efficiency of grease recovery by acid-cracking increased with a decrease in temperature. However, it was found in a more recent investigation<sup>120</sup>, that by boiling acidified effluent for a period of time complete destabilisation could be achieved, allowing suspended solids and grease to co-precipitate and form a free-draining floc with good potential for successful filtration. The amount of sulphuric acid required varied between 0,1 to 0,5% (by mass), the aim being maintaining the system at a pH below 3.

Optimum conditions for destabilisation occurred when boiling of the acidified effluent was maintained for not more than a quarter of an hour and it was subsequently cooled to 60 to 65°C before it was allowed to settle for half an hour. The sludge obtained was found to be voluminous (20 to 33% of the original volume), the voluminosity increasing with an increase in the suint content of the effluent and decreasing with an increase in the suspended solids content of the liquor<sup>78</sup>.

The supernatant liquor from this treatment contained as little as 200 mg/ℓ residual grease, 2 000 mg/ℓ BOD<sub>5</sub> and negligible quantities of suspended solids. A subsequently published work<sup>125</sup> of a pilot treatment plant constructed in the USA which incorporated this type of flocculation technique would appear to substantiate these findings.

The above investigation led to the development of an industrial process known at present as the 'Hot Acid Flocculation' process<sup>126-129</sup>. Wool scouring wastes are destabilised by a 10 to 15 minutes reaction at boiling point with sulphuric acid at a pH of 3, consolidation of the partially-cooled acidified contaminants into a settleable, free draining floc being achieved by addition of about 3 ppm of a cationic polyelectrolyte. This is followed by compaction of the floc and decantation of a clear supernatant effluent by gravity thickening, further dewatering of the compacted floc into a sludge for disposal with a separator consisting of a rotating perforated drum covered with a flexible sheet of plastic sponge (able to partially dewater sludge by water absorption) and neutralisation of the effluent with alkali. Recovery of crude lanoline from the sludge by liquid-liquid extraction with trichloroethylene and subsequent extraction of lanoline and soaps from crude lanoline with methanol and caustic soda using free falling film evaporators has also been suggested<sup>127,130</sup> and the respective process and its economics have been published<sup>131,132</sup>.

The 'Hot Acid Flocculation' process was successfully run on a pilot scale and subsequently full commercial installations were completed in two Australian mills<sup>133</sup>. This was followed by a full commercial installation in the United Kingdom. During full scale trials it was found that the particular separator used for dewatering was not capable of handling the amount of sludge presented to it and it was replaced by a horizontal decanter centrifuge capable of producing spadeable sludges having a high total solids content<sup>96</sup>. A flow diagram of the industrial process is shown in Fig. 7.

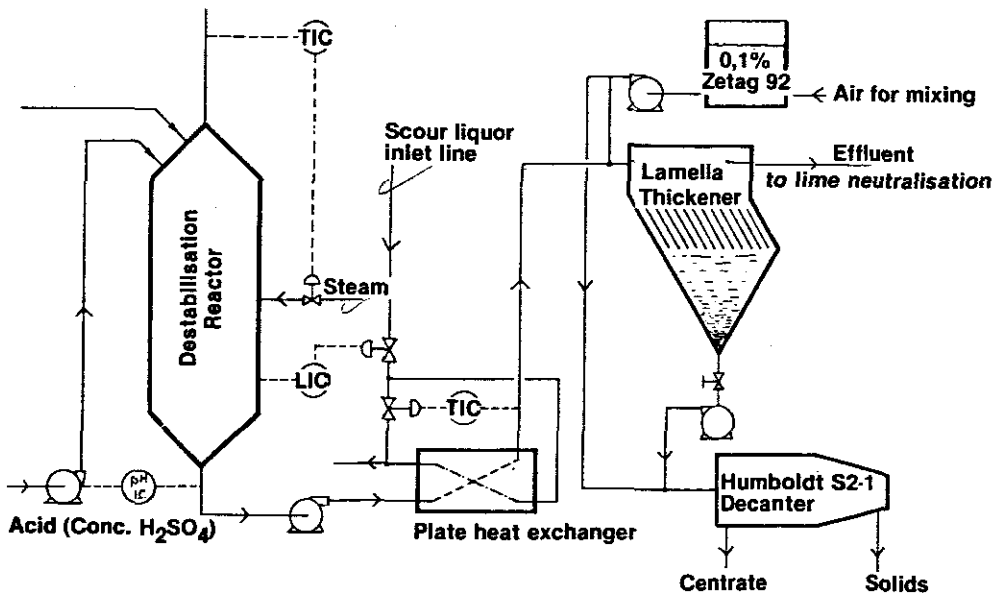


FIGURE 7  
Flow diagram of the 'Hot Acid Flocculation' process<sup>94</sup>

The latest version of this industrial process has been reported<sup>134</sup> to comprise a storage tank from where the scouring liquor is pumped, together with the centrate stream returning from the horizontal decanter centrifuge, through a plate heat exchanger (where it is heated to 90°C) into a destabilisation reactor. Continuous metering of sulphuric acid into the reactor allows automatic control of the pH at a value of 3. The height of the liquid in the destabilisation reactor is also controlled automatically by means of a centrifugal pump. The hot destabilised liquor is subsequently pumped through the plate heat exchanger (where it is cooled to 65 to 70°C), passed into a special cyclone mixer (where it is dosed with a 0,05 to 0,1% solution of a cationic polyelectrolyte) and then injected into a gravity clarifier/thickener (which allows the separation of a liquid sludge from a supernatant liquor). The liquid sludge is dewatered in a horizontal decanter centrifuge of the co-current type, thus producing a solid sludge (moisture content as low as 40%) suitable for (1) land disposal, (2) incineration or (3) solvent grease extraction. The effluent from the plant is neutralised to a pH of 6 to 8 with a solution of caustic soda. The results of trials conducted with 2 m<sup>3</sup>/h pilot plants, installed both in Australian and British Mills have successfully demonstrated the feasibility of a commercial treatment process<sup>134</sup>.

A very recent study<sup>135</sup> carried out at the CSIRO centre has shown that the

process comprising hot acid-cracking followed by centrifuging is capable of significantly lowering the levels of chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) of wool scouring liquors. However, this is not so in the case of liquors containing high suint concentrations, apparently due to a lack of removal of soluble contaminants by this process<sup>135</sup>.

Another major general problem involving 'acid cracked' effluents is the high level of sulphate. In many countries, the amount of sulphate that can be discharged to the sewer is limited to from 300 to 600 mg/l<sup>136</sup>. This stringent regulation is reported to be due to the effect of sulphate ions on the wastewater reticulation system. They form sulphate-aluminate complexes that swell and crack concrete made from nonresistant cement<sup>136,137</sup>. Furthermore, the concentration of sulphate is proportional to the amount of hydrogen sulphide that can be generated under anaerobic conditions<sup>138</sup>. Investigation<sup>136</sup> showed that sulphate levels in wool scouring wastes obtained from wool carbonising could be successfully reduced (by about 80%) by addition of aluminium chlorohydrate and lime at a pH of 10 to form an insoluble complex. The amounts of chemical agents used to remove 1 000 mg/l sulphate were 1 800 and 3 800 mg/l, respectively. Residual sulphate levels of 350 mg/l were obtained.

### 3.4 Chemical Flocculation

This technique has been widely used for treatment of wool and mohair scouring wastes. A variety of chemical agents were found to destabilise the emulsion, thus allowing purification of the scouring wastes.

Where detergents possessing ionic characteristics were used in the emulsification of grease, the separation of the dispersed phase particles from the aqueous phase was simplified by the use of these agents which modify these detergents to cause (1) a change in interfacial tension between these phases or (2) modify the electrical charges on the individual particles or (3) produce both effects<sup>120</sup>. Such modification results in size enlargement of the grease particles by a process known as flocculation in which the individual particles are attracted to each other by mild, but persistent forces. Flocculation permits gravity settling to proceed at a faster rate but produces a more voluminous sedimentation layer. Electrolytes, particularly those which furnish polyvalent ions (such as salts of trivalent aluminium and iron ions), polyelectrolytes or change in the pH of the system (such as by sulphuric acid or hydrated lime additions) have often been used successfully in bringing about the desired degree of flocculation<sup>120</sup>.

Where nonionic detergents were used in the emulsification of grease, two factors were reported<sup>129</sup> to appear to contribute to destabilising the colloidal protection of the detergent molecule, i.e. (1) the insolubility of the detergent, especially in the presence of cations and (2) the conversion of suint soaps to insoluble free fatty acids.

Chronologically, the first known development in the field of chemical flocculation occurred in 1925, when the use of lime and chloride<sup>139,140</sup> for treatment of wool scouring wastes was investigated. In the late 1930's and during the 1940's treatment by lime and carbon dioxide<sup>141</sup> and calcium hypochlorite<sup>105,106,142-144</sup> was investigated, the latter being applied subsequently for industrial uses. In the late 1940's the use of calcium chloride<sup>67,74,108,145-150</sup> was studied and subsequently, in the next decade or so, a change from the use of flocculating agents based on calcium to those based on aluminium occurred. During that period and virtually until 1970 the use of aluminium sulphate or alum<sup>150-154,164,166</sup> and hydrated aluminium silicate or bentonite<sup>82,155</sup> as flocculants was profusely studied. During the previous decade some of the previously mentioned flocculants were studied further whereas a new range of flocculants, comprising zinc hydroxide<sup>156</sup>, ferrous sulphate (combined with lime and wood flour)<sup>71,72,74,84,150,157-162,167</sup>, sodium chloride<sup>149,195</sup>, ferric chloride<sup>114,149,150,153</sup> and aluminium chlorohydrate<sup>114</sup> were investigated. These were very often combined with polyelectrolytes<sup>98,99,116,163,164</sup> whose role in flocculation is mainly to bring about a bridging effect during the coagulation stage.

The WRONZ Comprehensive Scouring system<sup>165-187</sup>, the CSIRO Lo-Flo system<sup>188-195</sup> and IWS Mini-Flo system<sup>95,196</sup> are modern processes which were basically created on the principles of (1) sludge treatment with the aid of polyelectrolytes, (2) artificial 'auto-flocculation' of wool scouring wastes by means of concentration of suint and scouring additives in the scouring liquor and (3) both developments combined, respectively. Lastly, ideas such as seawater<sup>197-201</sup> as a flocculant for wool scouring wastes led to two other flocculants i.e. bitterns<sup>202-206</sup> and magnesium chloride<sup>210,211</sup> which form the basis of the SAWTRI BITFLOC process. A summarised description of the main processes, classified according to the various chemical agents used for flocculation is given below:

#### **3.4.1 Lime and chlorine**

Gaseous chlorine was used to destabilise wool scouring wastes in the presence of lime<sup>139,140</sup>. Wool grease was extracted and bleached. The invention, known as the Raeve's process, was never applied in its original form.

#### **3.4.2 Lime and carbon dioxide**

Cold wool scouring wastes were treated with an excess of lime and then carbon dioxide was bubbled through the mixture reducing the pH to 5<sup>141</sup>. Sludge was collected and pressed under mild conditions (50°C and 200 kPa) to avoid wool grease passing through the filter. The residue was extracted with benzene, water was continuously separated by azeotropic distillation and crude grease recovered by removal of the solvent. The crude grease obtained was harder and lower in quality than the acid-cracked grease (see Section 3.3). The press cake could be used as fertilizer. The process, however, had no commercial application.

### 3.4.3 Calcium hypochlorite

The following process was reported<sup>143</sup> to have operated in the USA: Wool scouring wastes were pumped into a special storage tank in which they were continuously recirculated. Calcium hypochlorite was added in excess to the amount needed to neutralise the alkali, and the mixture was agitated by means of compressed air. After settling for 8 hours, the clean middle phase was discharged directly into the river. The combined top and bottom phases were acidified to a pH of 4 to 5, agitated, again settled for 8 hours and the clean supernatant liquor discharged into the river. The sludge was then pre-heated and hot pressed and wool grease containing some filtrate was separated by flotation and dried by heating with steam coils. Only 2% of the original grease remained unextracted by this process compared with 5 to 10% in the acid-cracking process. Similarly, the calcium hypochlorite process produced a filter cake with a residual moisture content of 15 to 25% and a grease content of 17%. The colour of the crude grease was reported<sup>143</sup> to be yellow to yellowish-brown for the calcium hypochlorite process compared with brown to dark brown for the acid-cracking process.

### 3.4.4 Calcium chloride

Originally, the industrial process for treatment of wool scouring wastes with calcium chloride<sup>108</sup> involved addition of carbon dioxide (similar to the lime and carbon dioxide process described in section 3.4.2) but the pH of the soap scouring wastes was only lowered to about 8 prior to the addition of the flocculant. Optimum concentrations of the flocculant of 1,2 to 1,6% (on scouring waste volume basis) were used. The treatment successfully reduced the BOD by 70%, grease content by 90% and suspended solids content by 98%<sup>108</sup>.

A commercial plant operating in the UK, later reported<sup>146</sup> the use of calcium chloride at an optimum concentration of 0,7% (on scouring waste volume basis) as flocculating agent. Waste purification was seen as the main aim, and the destabilisation of the emulsion was reportedly caused by precipitation of organic and inorganic salts of calcium<sup>146</sup>. After filtration through a rotary vacuum filter, the filtrate was discharged to the drain. The residual concentration of the different contaminants (BOD, grease and suspended solids) in the filtrate was found to be significantly lower than that of a typically purified stream from an acid-cracking plant<sup>146</sup>.

In two more recent investigations into flocculation by calcium chloride<sup>149,150</sup>, it was found that wool scouring wastes stabilised by nonionic detergents could be successfully destabilised. A flocculant concentration of only 0,3%<sup>149</sup> (on scouring waste volume basis) and a pH value of about 5,<sup>150</sup> seemed optimum. However, the volume of sludge produced by the treatment significantly increased with an increase in flocculant addition from 0,1 to 0,5%<sup>150</sup>.



### 3.4.5 Alum

Flocculation of wool scouring wastes by alum was described in a patent<sup>152</sup>. In this process, alum was added to wool scouring wastes, and when necessary, the pH of the scouring wastes was lowered to some value in the range of 5 to 6.5. The sludge phase, which had separated out after 8 hours settling and which contained most of the grease and virtually all of the suspended solids, was heated and filtered in a filter press. The supernatant liquor obtained by settling was directly discharged to the drain. During the filtration stage, a suspension rich in grease was obtained and wool grease was recovered from this suspension by centrifuging. The filter cake was disposed of by incineration or used as a fertilizer. The recovery of alum by treatment with sulphuric acid after centrifuging was also suggested<sup>166</sup>.

During a more recent investigation, Anderson et al<sup>164</sup>, found that the addition of 2 000 mg/l alum combined with 50 mg/l of a cationic polyelectrolyte caused a decrease in grease and suspended solids contents of the supernatant liquor of 65 and 83%, respectively, at pH 5 and of 60 and 75% at pH 6. Furthermore, biological pretreatment lowered the grease and suspended solids contents of the supernatant liquor to 9 to 15% and 5 to 10% of their original level, respectively. Flocculation (15 to 20 minutes residence time) was performed at room temperature. Moreover, it was found in a subsequent study<sup>165</sup> that heating an alum sludge tends to reduce its volume or, in other words, settling rate and sludge volume are improved with increasing temperature. In all the experiments performed during the above investigation, the treatment temperature for sludge separation was 60°C, both because this temperature could be more easily attained in a heat exchanger and because it was sufficient to produce the desired sludge characteristics. The investigation also showed that flocculation by alum produces sludges which dewater more easily than those produced by an acid treatment alone to the same pH<sup>165</sup>.

In a subsequent investigation<sup>150</sup>, it was shown that alum was the most effective flocculating agent from the range investigated, particularly at a pH value close to 5. The other flocculating agents studied were ferric chloride, calcium chloride and ferrous sulphate. A COD (chemical oxygen demand) removal of 80% was achieved by addition of about 0,8% of alum. The study<sup>150</sup> also indicated that an increase in temperature from 20 to 60°C could be detrimental to the degree of destabilisation of the emulsion, with grease removal decreasing accordingly from 55 to 35%.

### 3.4.6 Bentonite

This flocculation process was developed mainly with the aim of purifying wool scouring wastes. The pH was adjusted to 5 with acetic acid and subsequently bentonite was added in concentrations of 0,1 to 0,5%. Good destabilisation of the emulsion was obtained and figures for grease removal of as high as 96% were recorded. There was some similarity between this treat-

ment and acid cracking but its efficiency seemed to be higher than that of the latter.

#### **3.4.7 Zinc hydroxide**

Flocculation of wool scouring wastes with zinc hydroxide was investigated in Japan<sup>156</sup>. Zinc hydroxide was reported to be a better coagulant than alum, ferrous sulphate or ferrous chloride. Moreover, zinc hydroxide could be successfully recovered from the filter cake obtained by flocculation followed by filtration (by means of the so called 'roasting' of the sludge) and subsequently recycled into the process, thus lowering costs considerably.

#### **3.4.8 Ferrous sulphate**

An industrial process, named Traflo-W<sup>84,158,159</sup>, was developed in the laboratories of Wira. It involved treatment of wool scouring wastes with a combination of a mineral acid, ferrous sulphate, lime and wood flour. The pH of wool scouring wastes was adjusted to 6, the ferrous sulphate solution was then added and the pH adjusted back to a value of 7,5 to 8. Wood flour was then added to the treatment tank and the contents stirred to keep solid matter in suspension. After one hour of flocculation the treated waste was filtered through a rotary vacuum filter. A reduction in permanganate value (PV) of the original wastes from approximately 2 000 to 100 mg/ℓ was reported<sup>158</sup>.

An experimental plant was installed by Wira<sup>167</sup> and comprised a treatment tank with a suitable stirrer blade and a rotary vacuum filter using filter cloth and filter aids. This process has been implemented on a commercial basis in various mills in the UK and France and it has been reported<sup>95</sup> that reductions in COD levels of as much as 97% have been achieved on wool scouring wastes.

#### **3.4.9 Sodium chloride**

The use of common salt for flocculating wool scouring wastes was not investigated until the previous decade, mainly because of the theoretical consideration<sup>161</sup> that salts of a trivalent metal should show a hundredfold efficiency when compared to those of a divalent metal and the latter a hundredfold efficiency when compared to those of a monovalent metal (i.e. sodium or potassium). In practice, however, it was found<sup>149</sup> that a reduction in grease content of around 45% could be achieved by an addition of 0,9% (m/v) sodium chloride to wool scouring wastes and later it was shown<sup>195</sup> that nearly 2% (m/v) sodium chloride is needed to fully destabilise the emulsion.

#### **3.4.10 Ferric chloride**

It has been shown<sup>149,150</sup> that a substantial reduction in grease could be achieved by an addition of 0,5 to 0,8% (m/v) ferric chloride to wool scouring wastes and could bring about a percentage removal of COD as large as 80%. An optimum pH for flocculation of about 5,5 was reported<sup>150</sup>. The results of these investigations<sup>149,150</sup> indicated that, in addition to a 'flocculation range' of coagulant concentration, a 'precipitation range' due to a salting-out effect was present.

### 3.4.11 Aluminium chlorohydrate

An investigation into the effectiveness of salts of trivalent metals<sup>114</sup> (aluminium and iron) showed that if alum (which was found to be the best of these<sup>150</sup>) was eliminated from the list because of factors such as limitation on sulphate content of treated wastes and excessive acid usage for pH correction, two others required examination, i.e. ferric chloride and aluminium chlorohydrate. It was shown<sup>114</sup> that a higher concentration of the former was required to achieve the same degree of treatment as that achieved by the latter, but the former being a more acid salt gave a higher degree of alkali neutralisation resulting in a reduced acid requirement. In addition, the aluminium chlorohydrate gave a lighter floc and a drier sludge than ferric chloride<sup>114</sup>. When addition of flocculant was combined with electroflotation (see section 3.2) the lighter floc obtained reduced retention time required in the flotation chamber and, therefore, a more compact plant could be offered in the case of the latter as compared with the former. On balance, the aluminium chlorohydrate system was more favourable than the ferric chloride one, in spite of the former flocculant being more expensive.

### 3.4.12 Polyelectrolytes

Over the past few years the use of synthetic flocculants for water treatment has increased rapidly. These flocculants are relatively high molecular weight polymers with large ionisable sites along the chain. In low concentrations (of the order of a few mg/l) they bridge between the colloidal matter in the liquor causing aggregation and settling. The flocculated material can then be removed.

After testing more than 160 commercially available polyelectrolytes, McLachlan, Smith and Webb<sup>116</sup> found that a small group of cationic and nonionic polyacrylamides flocculated *wool scouring wastes* at a concentration of 5 to 10 mg/l, reducing the suspended solids concentration by 40 to 70% and the grease concentration by 10 to 30%. The advantage of using a polyelectrolyte was that the liquor could be treated during the scouring process and then returned to the scouring bowl, which was not always possible with other methods of chemical treatment.

Continuing the investigation concerning treatment of wool scouring wastes by polyelectrolytes alone, McLachlan<sup>163</sup> found that their ability to flocculate contaminants such as grease and suspended solids was highly specific. Since many of the cationic and nonionic polyelectrolytes did not cause flocculation, yet apparently had similarly charged chemical groups, the ability to cause flocculation appeared to be related to the configuration of the polymer in solution. The greater the molecular weight of the polymer, in a certain range of flocculants, the more efficient was the removal of grease and suspended solids.

As mentioned elsewhere, it was found<sup>164</sup> that treatment by alum (2 000 mg/l) and a cationic polyelectrolyte (50 mg/l) resulted in a reduction in the

grease level of the supernatant liquor of 60% at a pH of 6 and 65% at a pH of 5. A more recent investigation<sup>99</sup> revealed that polyelectrolytes could significantly improve flocculation, particularly under mild acid conditions, e.g. pH 6. Addition of alum alone (1 000 mg/l) to wool scouring wastes reduced the COD by up to 45% whereas a further addition of a cationic polyelectrolyte (20 mg/l) increased this figure to 60%.

Another investigation into the use of electrolytes combined with polyelectrolytes for flocculation of wool scouring wastes<sup>98</sup> revealed that adding an anionic polyelectrolyte in concentrations of up to 50 mg/l to wool scouring wastes pretreated with ferric chloride improved the flocculation efficiency causing a reduction in the grease level of the supernatant liquor from 32 to about 50%. Furthermore, the same investigation showed that a reduction in the grease level of the supernatant liquor could be obtained by adding 10 mg/l of a cationic polyelectrolyte to wool scouring wastes pretreated with 6 000 mg/l calcium chloride. Another aspect related to the use of polyelectrolytes<sup>98</sup> is the reduction in sludge volume. In the latter case, a rather small polyelectrolyte addition (10 mg/l) resulted in a reduction in sludge volume from approximately 45 to 30% (v/v).

Research into the field of waste treatment, particularly in the area of flocculation by means of polyelectrolytes, has evolved in the last decade to the development of a modified system of emulsion scouring of raw wool and waste treatment, often referred to as the WRONZ Comprehensive Scouring system<sup>165-184</sup>. Basically, this system enables scouring of raw wool to proceed continuously for longer periods than those normally obtained in more conventional systems, mainly due to 'in-house' circulation and purification of the first scouring bowl liquor. The waste treatment system, which has been modified during the last years, involves the continuous removal of heavy settleable solids<sup>94,185,186</sup>, increased recovery of wool grease<sup>166,169,172,182</sup> and heat<sup>112,168,173</sup>. Plants have been in successful operation in many parts of the world. Water consumption of 3,0 to 3,5 litres per kg raw wool and grease recoveries of about 50% have been reported<sup>170</sup> for fine wools.

Commercial trials have been in progress for some time on the dewatering of sludge from the heavy solids tank (HST) by means of a horizontal decanter centrifuge, the most efficient removal being achieved when a polyelectrolyte flocculant was added to the liquor prior to settling. The latter improved the removal of suspended solids from 51 to 79%<sup>171</sup>.

More recent studies<sup>186</sup>, however, have shown that when semi-industrial trials were performed using a horizontal decanter centrifuge of the co-current type, suspended solids removal averaged 68 to 75%. The total solids content of the decanter sludge was only 46% when no polyelectrolyte was added and this level further decreased to 41% when polyelectrolyte was added. Decreasing the bowl speed of the decanter centrifuge, i.e. the centrifugal force, had no significant effect on the suspended solids removal. Moreover, the addition of floccu-

lant to the liquor being fed to the HST prior to the decanter had no effect on the suspended solids removal but gave a decrease in sludge consistency<sup>186</sup>. The latest version of the WRONZ Comprehensive Scouring system, which attempts to eliminate the problems encountered previously, is as illustrated in Fig. 8.

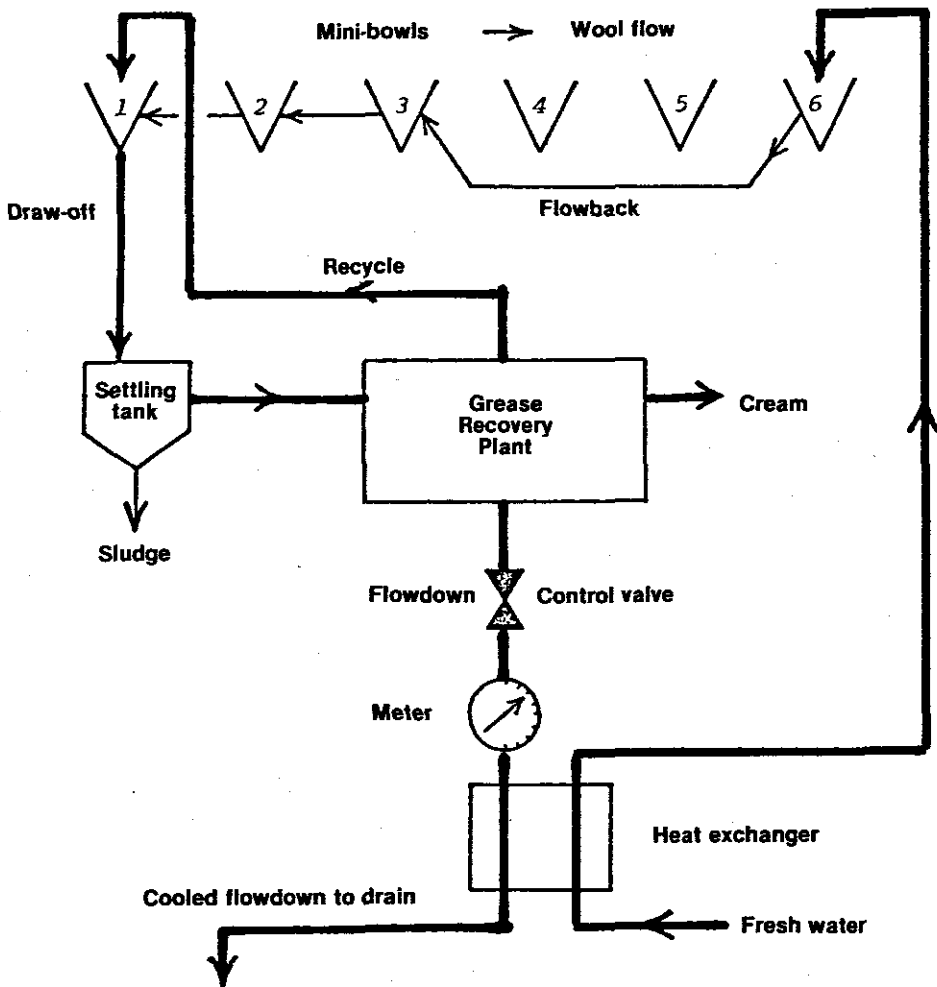


FIGURE 8  
Simplified flow diagram of the WRONZ Comprehensive Scouring System<sup>184</sup>

The original WRONZ scouring train has also lately been modified (see Fig. 8) by replacement of the scouring bowls by smaller bowls or mini-bowls<sup>177,178,187</sup>. These are being used in conjunction with dirt and fibre removal in an attempt to improve the removal efficiency and achieve zero flowdown. One aim of scouring in this way is to operate in very concentrated liquors, as with the Lo-Flo process, and with a potentially greater recovery of wool grease. In general, WRONZ plants have been operating for several years in various mills around the world and the process seems to have good prospects of further commercialisation in the future.

### *3.4.13 Suint and detergent chemicals*

The suint salts present in wool scouring wastes were found<sup>188</sup> to destabilise the emulsion when their concentration reached a certain level. This finding led to the development of an industrial process for treatment of wool scouring wastes known as the CSIRO Lo-Flo process. In this process the concentration of suint and detergent chemicals is allowed to build up quickly beyond a certain level by restricting the water input into the Lo-Flo unit which is designed to replace or supplement the first bowl of a conventional scouring train<sup>188,189</sup>. The liquor from the unit is passed through two centrifuges (decanter and disc type in series) where the bulk of the impurities is removed. A high-solids sludge is obtained from the first of the centrifuges and grease is recovered in high yield (70 to 80%) from the second. The only effluent evolving from the process is rinse water which would normally be acceptable for discharge to sewer without attracting high charges. The economics of this process is reported to be better than that of other processes<sup>188,189</sup>.

This process has been implemented on a trial basis at two commercial scouring mills. An alternative schematic arrangement of the Lo-Flo system applied to a conventional industrial scouring train is shown in Fig. 9. The scouring efficiency of two Lo-Flo mini-bowls has been investigated<sup>177,178,183</sup> and it has been shown to be similar to that of two bowls of conventional length.

The Lo-Flo process has undergone modifications in the last few years. An experimental eight-bowl scouring machine, comprising a three mini-bowl unit followed by five other conventional bowls, was installed at CSIRO<sup>191</sup>. Pilot scale investigations<sup>192,194</sup> in this experimental plant have shown that the preferred operating method is to use sodium sulphate and detergent for scouring. Typically, 90% of the grease and suint were removed in the Lo-Flo unit, and with some modifications to the conventional bowls, 90% of the suspended solids could also be recovered<sup>194</sup>. Wool grease recoveries varied from 50 to 90% and detergent consumptions from one-half to two-thirds of that in normal scouring. The eight-bowl Geelong (CSIRO) plant has been operated for a considerable time with an overflow from the final rinse bowl only, yielding, therefore, an effluent with a marginal BOD level. The implications of stopping the rinse water overflow to give zero-discharge operating conditions have not yet been studied<sup>194</sup>.

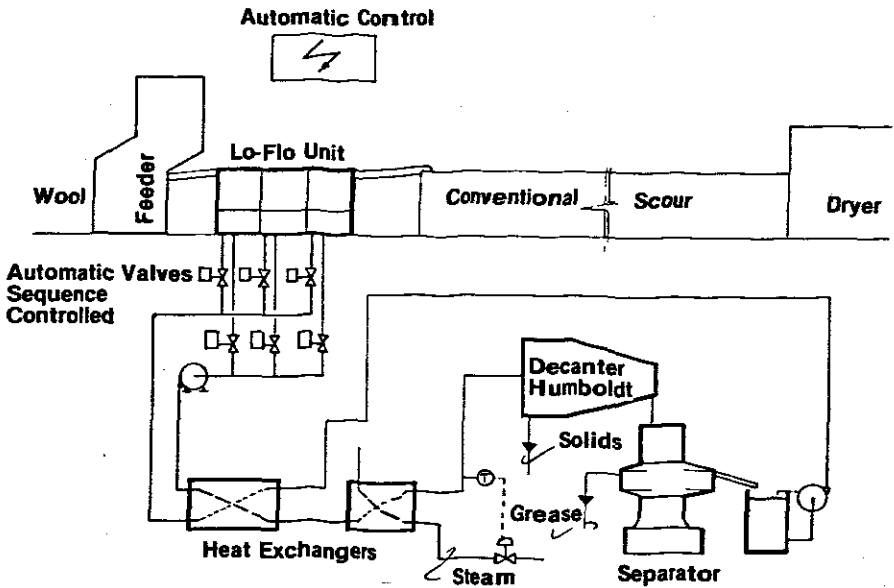


FIGURE 9

An alternative schematic arrangement of the Lo-Flo system applied to a conventional industrial scouring train<sup>94</sup>

This pilot plant work has been accompanied by some more basic work<sup>193,195</sup> on the mechanism of emulsion destabilisation of the Lo-Flo system. The results of these studies indicated that coagulation due to 'salting-out' of the nonionic surfactant by electrolytes present in the Lo-Flo liquors (such as suint salts and sodium sulphate which is used for scouring) is the most important destabilising mechanism, but that density effects are of paramount importance in determining whether the solids load of these liquors will settle downwards (flocculation) or upwards (flotation)<sup>195</sup>.

The IWS has lately completed the development of a process which has been called the Mini-Flo process<sup>95,196</sup> (illustrated in Fig. 10). Basically, the Mini-Flo process is a 'marriage' between the Australian Lo-Flo and the New Zealand WRONZ mini-bowl processes. It consists mainly of a three wash-plate unit (Lo-Flo system), a two self-cleaning mini-bowls unit (WRONZ-system) and an additional pair of mini-bowls<sup>196</sup>. The first set of scouring bowls is mainly intended for the removal of grease and suint from raw wool and for the recovery of grease. The second set of scouring bowls is mainly intended for dirt removal from raw wool and sludge removal from the scouring bowl. The third set of bowls is used for rinsing.

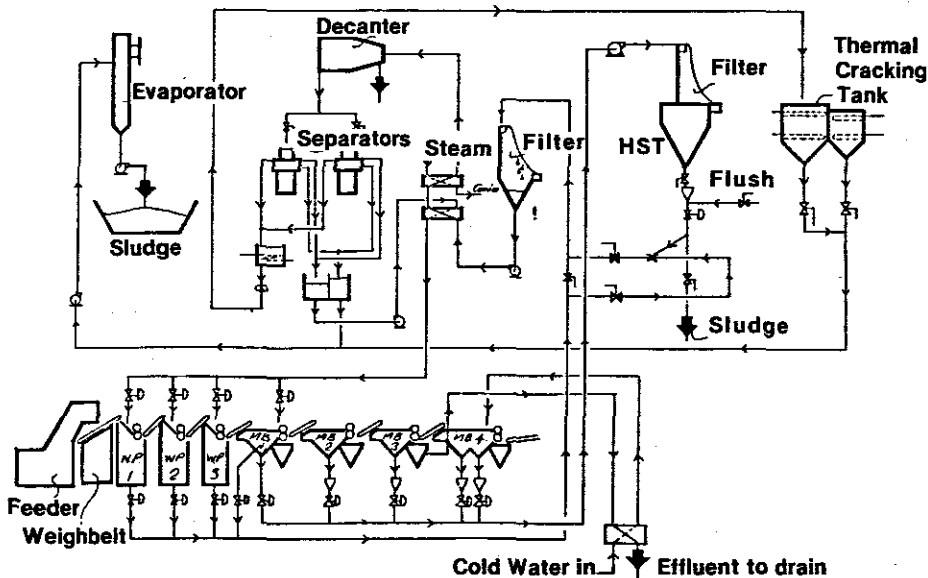


FIGURE 10

Schematic flow diagram of the latest version of the Mini-Flo process.

The liquor from the Lo-Flo unit is screened through a filter for fibre removal and de-sanded through a horizontal decanter centrifuge and grease is recovered by passage through separator centrifuges, thermal cracking and secondary centrifuging. The grease recovery process produces a dirt contaminated grease (grease recovery efficiency 65 to 70%). This grease can be bleached to yield a good quality grease, the final grease recovery efficiency, nevertheless, remaining at a relatively high level (52%). An interesting feature of this grease recovery process is the thermocracking stage. During this process the top of the thermocracking tank is maintained at 95°C while the temperature in the middle is 80°C and at the bottom 75°C.

With reference to Fig. 10 again, a Trimwaste device (Ultrasonic Sludge Blanket Detector) has been installed at the bottom of each of the mini-bowls (WRONZ system) used for scouring and a scanner allows for regular withdrawal of sludge from these scouring bowls into the HST tank, which is also equipped with a Trimwaste device. The sludge from the HST tank is then fed into the horizontal decanter centrifuge through a filter while the overflow liquor from the HST tank is fed into the grease recovery plant. An evaporator has been added to the Mini-Flo process to deal with liquid sludges originating from the centrifugal separators and the thermocracking plant<sup>196</sup>. In general, the process has been applied on an experimental basis in several mills in the UK and seems to hold good prospects of commercialisation for the future.



### 3.4.14 Sea-water

Laboratory investigations into destabilisation of wool and mohair scouring wastes with sea-water<sup>197,198,201</sup> showed that it can be used to treat liquid sludges originating from primary centrifuging of liquors to the extent of almost 100% grease removal, as well as other types of wastes i.e. liquors and effluents, to the extent of at least 80% grease removal, provided centrifugal aid is provided in all cases. It was also found, however, that large volumes of sea-water (nearly 0,7 l for every litre of waste) and long periods of storage prior to centrifuging (4 to 7 days) were required for optimal treatment of liquors and effluents.

A further laboratory study<sup>199</sup> showed that three major constituents of sea-water, namely *sodium chloride*, *magnesium chloride* and *magnesium sulphate* were mainly responsible for the destabilising effect of sea-water on wool scouring wastes.

Finally, a pilot investigation<sup>200</sup> into destabilisation of sludges with sea-water revealed that 80 to 90% of the grease originally present could be removed in the form of a spadeable sludge (average total solids content 50%) when industrial sludges were treated with equal volumes of sea-water and then passed through a horizontal decanter centrifuge (of the counter-current type) and disc centrifuge in series. Storage of the sludge for several days at 65°C prior to centrifuging improved grease removal to a level of nearly 95%, thus producing an aqueous stream with a residual grease content of 600 mg/l. The large amounts of sea-water required for this process, however, rendered it as impractical for purposes of commercial application.

### 3.4.15 Bitterns

Following the research work on sea-water carried out at SAWTRI, concerted attempts were made at this research establishment to find a concentrated solution based on the same constituents of sea-water (i.e. sodium chloride, magnesium chloride and magnesium sulphate<sup>199</sup>), which would make possible the use of much reduced amounts of flocculant for destabilisation. It was found that bitterns, i.e. a magnesium-rich waste product of little commercial value, derived from a common-salt recovery plant (Table 6), would most likely suit these conditions.

Laboratory studies<sup>202-205</sup> clearly showed that bitterns was an extremely effective natural flocculant for liquid sludges and effluents originating from a centrifugal grease recovery plant. Grease removal efficiencies of 95 to 100% were obtained in both cases by treatment with 5% (v/v) bitterns followed by centrifuging (1 000 to 2 000 G).

Pilot scale studies<sup>206</sup> were carried out using a horizontal decanter centrifuge of the co-current type. These studies showed that when liquid sludges from secondary settling of wool scouring liquors, which are difficult to destabilise, were treated with 5% (v/v) bitterns about 10 minutes prior to

**TABLE 6**  
**TYPICAL COMPOSITION OF BITTERNs**

CONSTITUENT	CONCENTRATION (%)
NaCl	31,6
MgCl <sub>2</sub>	7,5
MgSO <sub>4</sub>	6,5
CaSO <sub>4</sub>	0,1
Compounds of K <sup>+</sup> I <sup>-</sup> and Br <sup>-</sup> + halophilic bacteria	0,3
H <sub>2</sub> O	54,0
Total	100,0

entering the horizontal decanter centrifuge, the solid discharge or decanter sludge contained over 70% of the grease and nearly 90% of the suspended solids originally present. In addition, significant reductions in the levels of bacterial count and chemical oxygen demand were obtained in the aqueous discharge from the horizontal decanter centrifuge (centrate). In general, the products of this treatment were a centrate of reasonably low residual grease content and a decanter sludge rich in grease and of spadeable consistency (total solids content 60%). No visible wear of the screw flights of the horizontal decanter was noticed after a few months of continuous operation<sup>206</sup>.

#### **3.4.16 Magnesium chloride**

The treatment of wool scouring wastes with bitterns seemed suitable for mills located nearby a source of bitterns, but from an economical point of view the viability of the process would be dependent upon several factors, such as transport costs for flocculant (particularly for factories not located nearby a common-salt recovery plant), on municipal charges for sewer acceptance<sup>207</sup>, etc. It was important, therefore, to find a substitute for bitterns. Since the active constituent of bitterns was shown<sup>199</sup> to be the magnesium salts, SAWTRI embarked on the evaluation of magnesium chloride flakes. Because of its relatively low price and the fact that it is a fairly pure commercially available product containing only trace quantities (< 1%) of sulphate, sodium and potassium<sup>208,209</sup>, which is desirable from the point of view of disposal into municipal sewers<sup>207</sup>, it was considered a suitable substitute for bitterns.

Laboratory studies<sup>210</sup> confirmed that magnesium chloride, which is available commercially in the form of flakes<sup>208,209</sup>, is a good substitute for bitterns as a flocculant for wool and mohair scouring wastes and, particularly, for liquid sludges. The process involving destabilisation of liquid sludge with either of these flocculants i.e. bitterns or magnesium chloride and subsequent

dewatering by passage through a horizontal decanter centrifuge, which has been called the SAWTRI BITFLOC process<sup>211</sup>, is illustrated schematically in Fig. 11.

Pilot scale studies using this process<sup>210,211</sup> have revealed that an addition of 1% (m/v) magnesium chloride gives slightly better results than those obtained with a 5% (v/v) addition of bitterns. Typical performance levels of the horizontal decanter centrifuge were found to be a grease removal of 80%, a suspended solids removal of over 90%, a 68% reduction in chemical oxygen demand and an 88% reduction in bacterial count.

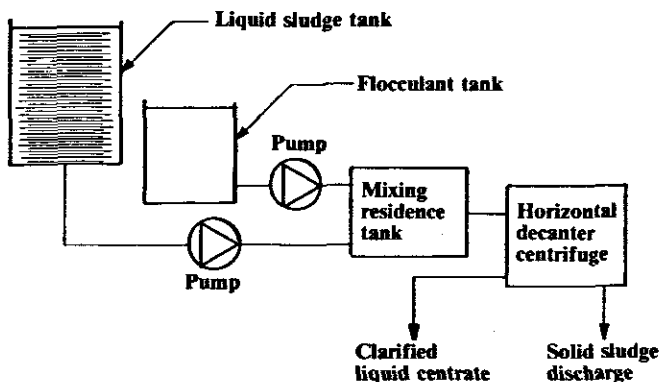


FIGURE 11

Schematic flow diagram of the SAWTRI BITFLOC process

### 3.5 Alcohol Destabilisation

Research work into the destabilisation of wool scouring wastes with aliphatic alcohols was only started in the late 1940's. In 1948, the use of butanol<sup>212</sup> was investigated and the subject of that study was extended later, in 1951, to include a variety of other alcohols<sup>213</sup>. Two other studies on the matter<sup>74,214</sup> were published in the early 1970's.

Initial studies<sup>213</sup> showed that the scouring efficiency of raw wool can markedly improve by addition of linear alcohols to the scouring liquor and that it can further improve by addition of sodium chloride combined with alcohol. This effect, however, required a minimum level of suint on the fibre. It was also found<sup>213</sup> that, when the concentration of alcohol was increased beyond certain levels (30% for methanol, 20% for ethanol, 10% for n-propanol, 3% for n-butanol, 2,5% for n-pentanol and 0,5% for n-hexanol), the emulsion was destabilised, yielding a grease-rich alcohol phase on top and a grease-free liquor saturated with alcohol phase in the bottom.

Following this finding, a further laboratory study<sup>213</sup> was carried out using

2% n-butanol in conjunction with sodium chloride for the treatment of wastes. Grease was recovered from the top alcohol phase using distillation and the residual liquor was filtered before it was purified from its alcohol content by the same procedure.

During another investigation<sup>74</sup>, the treatment of scouring wastes with n-hexanol was studied. It was shown that mixing of wastes with this alcohol followed by centrifuging produces three phases, namely a grease-rich alcohol phase, a liquor saturated with alcohol phase and a sludge/alcohol phase. The alcohol from the three phases was recovered by steam stripping, thus making possible the recovery of grease and recycle of liquor and alcohol.

A later investigation<sup>214</sup> showed that n-pentanol gives the best grease recovery (86%) when compared with n-butanol and n-hexanol. Grease recovery, in general, was better at a pH of 7 as compared with a pH of 10 and the acid value of the recovered grease varied with the pH of the liquor.

It was found later<sup>163</sup> that addition of a cationic polyelectrolyte (10 mg/l) after alcohol addition, significantly reduced the time required for phase separation from hours to practically seconds, causing an immediate separation of the grease-rich phase. During the same investigation<sup>163</sup>, the various alcohols were added to the scouring wastes at concentrations slightly above their solubility level in water. From the wide range of alcohols investigated, cyclohexanol, n-butanol and n-pentanol were reported to give the greatest grease removals. n-Pentanol was chosen for further study in spite of being slightly less effective, because of the lower concentration required and the consequently smaller volume to be later distilled from the treated waste<sup>163</sup>.

Further experiments<sup>163</sup> were carried out using n-pentanol and a cationic polyelectrolyte at 60°C over a wide range of waste compositions. It was found that grease removal was much more dependent on the suint level of the untreated waste than on its grease level. At low suint concentrations (less than 2.5%) the reduction in grease level increased from approximately 65 to 90% with a decrease in pentanol addition from 5 to 3% (v/v). At high suint concentrations (higher than 5%), however, the addition of 5% (v/v) pentanol gave the greater grease reduction (about 80%) in the range investigated. Furthermore, the pH of the waste had no effect on grease reduction, while an increase in temperature caused only a slight increase in grease reduction<sup>163</sup>.

All these studies<sup>74,163,213,214</sup> led to the development of the DSIR (New Zealand) Alcohol Destabilisation process which was patented<sup>215,216</sup> in 1977. The process comprises a preliminary flotation stage to remove part of the solids load, mixing of the treated liquor with sufficient (aliphatic or cyclic) alcohol to produce a concentration in excess of the saturation level in order to leave a discrete alcohol phase, addition of 2 to 20 mg/l of a cationic or nonionic polyelectrolyte to effect a liquid/liquid separation from the liquor by flotation followed by heating and finally, stripping the separated grease from the alcohol phase.

Results of a pilot scale study reported in the same patent<sup>215</sup> showed that the addition of a wide range of alcohols at 60°C, i.e. a variety of butanols, pentanols and cyclo-hexanols (10% v/v for the first, 4% v/v for the second and 3 to 4% v/v for the third type) and 5 mg/l of a cationic polyelectrolyte produced a reduction in the grease level of the mother waste sample of 50 to 95% and a reduction in suspended solids level of 50 to 85%.

These pilot scale studies have led to the implementation of the DSIR Alcohol Destabilisation process on an industrial scale at a wool scouring mill in New Zealand<sup>95,217</sup>. The last version of this process consists of alcohol destabilisation with n-pentanol and a polyelectrolyte to yield a grease-rich top alcohol phase, a middle phase containing essentially suint and a bottom phase containing essentially dirt. The three streams are then evaporated in packed columns to separate the various constituents<sup>95</sup>. The evaluation of plant performance has not been completed yet but it is expected to yield a 70 to 75% reduction in chemical oxygen demand and a grease removal of 80%<sup>95</sup>.

### 3.6 Solvent Extraction

Solvent extraction of wool scouring wastes has for a long time been considered a good way to recover the grease and hence, lowering the pollution load induced by these wastes. The practical application of this idea has been frequently attempted in the last fifty years or so but always failed because of one or a combination of the following factors: (1) poor recovery of grease due to emulsion formation, (2) excessive costs incurred due to large amounts of power required for solvent distillation and (3) a vain effort to prevent gross losses of solvent.

The history of this technique, as far as a methodical investigation is concerned dates back to 1953, when two patents<sup>218</sup> were granted for the protection of the solvent extraction process. Renewed attempts<sup>218</sup> were made on solvent extraction of wool scouring wastes using white spirit (b.p. 115 to 160°C). Two studies into the matter<sup>219,220</sup> revealed that 8% of the original solvent volume used for extraction remained in the aqueous phase as a solvent-in-water emulsion. It was subsequently found that this emulsion could be broken by centrifugal separation. Conclusive results from these studies<sup>219,220</sup> showed that excellent recovery of wool grease of good quality was possible using multi-stage extraction (up to 23 stages) and adequate recovery of solvent could be achieved when the organic and aqueous phases were separated by centrifuging. The economics of the process, however, was not assessed and no practical application of this study is known.

Some research work on solvent extraction<sup>221-225</sup> of wool scouring wastes was carried out during the early 1970's, the various investigations involving a wide variety of solvents. However, a final assessment of the efficiency of wool grease extraction by 1% (v/v) addition of benzine<sup>226</sup> revealed that in some cases it could be only about 15% higher than that obtained by conventional

centrifuging, thus rendering this process rather economically non-feasible. Another publication<sup>227</sup> showed agreement with these considerations, stressing that as far as the residual solvent content of the degreased wastes was concerned, one major difficulty was that the majority of the sewerage authorities around the world had set an extremely low limit on the discharge of volatile solvents. The removal of all detectable solvent from the degreased wastes before discharge was practically impossible.

An industrial process named the 'Sover' process was developed<sup>228-231</sup> in the 1970's in which the scouring of raw wool in solvent and simultaneous treatment of solvent liquors was carried out. In this process, scouring is carried out by transporting raw wool through a solvent extractor on a continuous perforated steel belt. Two solvents are used for scouring i.e. isopropyl alcohol mainly for the extraction of suint and dirt and hexane for the extraction of wool grease.

The effluent treatment facility of the Sover process<sup>229</sup> comprises a decantation tank for the removal of heavy solids, a lanoline refining plant for the further treatment of the upper hexane-rich phase and a distillation unit for isopropyl alcohol recovery from the lower alcohol-rich phase and production of cheap fertilizer by further evaporation of alcohol from the concentrate produced by distillation. The Sover process has been reported<sup>230,231</sup> to have commercial application in Belgium, USSR and Japan.

Two investigations<sup>232,233</sup> into the solvent extraction of wool grease from solid wool scouring sludges (with moisture contents of about 50%) revealed that a two-stage extraction process involving (1) extraction of crude grease and the simultaneous co-distillation and separation of water using a water-immiscible and low boiling point solvent such as trichloroethylene and (2) a hot binary-phase methanol extraction to separate the crude wool grease (after bleaching) into quality wool grease and crude soap compound, could yield a commercially viable process for lanoline production from sludge.

### 3.7 Biological Treatment

Biological digestion of wool scouring wastes has been investigated during the 1970's. Reductions of BOD under practical conditions approximately between 50 and 70% for strong scouring wastes have been reported<sup>234</sup>.

The various investigations into this technique fall into four categories, i.e. (1) biofiltration<sup>120,164,227,234-237</sup>, (2) activated sludge<sup>120,238,239</sup>, (3) anaerobic/aerobic digestion<sup>94,95,120,227,240,241</sup> and (4) land irrigation<sup>227</sup>. These categories will be dealt with separately, as follows:

#### 3.7.1. Biofiltration

Two types of systems have been investigated, i.e. the Flocor trickling filter and the rotating biological disc. Flocor trickling filters<sup>164</sup> consist of PVC modules with a large surface area, supported vertically by means of an arrangement of beams. These PVC modules, which replace the classical stone

beds used in sewage works, allow free passage of air through the waste liquor. The biomass which develops on the modules feeds on the pollutants present in the waste liquor, thus producing liquor purification.

The rotating biological disc<sup>164</sup> consists of a unit of discs closely mounted onto a horizontal shaft. The unit rotates just above the level of the waste liquor, a portion of it being in contact with the liquor and the remaining portion with the air. The biomass developed on the rotating disc can then alternatively feed on the pollutants present in the liquor and absorb oxygen from the air.

These two biological systems were both studied in two investigations<sup>164,235</sup> and results showed that neither the Flocor filters nor the rotating biodiscs can achieve high performance levels (i.e. > 90% reduction in contaminants level) unless treatment times were of the order of 24 hours. However, it was found<sup>164,236</sup> that a low-level biological treatment increased the efficiency of subsequent chemical flocculation treatment (see Section 3.4.5). It was reported<sup>236</sup> that a combined biological-chemical treatment yielded higher quality effluents than either of the two treatments individually and avoided sludge-handling problems associated with straight biological treatments. The biological pretreatment partially destabilised the waste without effecting a large reduction in the level of pollutants. It also increased the reduction in residual levels of grease and COD after chemical treatment from approximately 62 to 90% and 71 to 90%, respectively, at a pH of 5<sup>236,237</sup>.

The performance of a Flocor biofilter pilot plant was subsequently investigated<sup>120</sup> and it was found that independently of the influent waste flow rate (in the range of 150 to 250 l/hr), an overall reduction in grease level of only 25% and an overall reduction in suspended solids level of 61% could be achieved.

It was also reported<sup>227</sup> that a practical difficulty with the use of biological treatments for scouring wastes, in general, and biofilters in particular, is that they all produce fairly bulky sludges, seldom with a suspended solids content above 5%. Usually such liquid sludges cannot be dumped and must be dewatered by chemical or thermal treatments. Full plant trials on purification of scouring wastes by Flocor biofiltration have been in progress for the last five years<sup>234</sup>.

### **3.7.2 Activated sludge**

The activated sludge treatment used in sewage works has been applied in the last few years to wool scouring wastes. Investigations into this field<sup>120</sup>, first restricted to laboratory scale, have shown that the naturally occurring spores present in these kind of wastes are not able to develop and survive without the aid of added nutrients, a small reduction in BOD<sub>5</sub> level of these wastes from 2 740 to 2 240 mg/l being obtained in one specific case. Anaerobic conditions (self activated sludge) was found to be even less efficient than the previous treatment. It was furthermore proved that nutrient feed consisting of a

biodegradable detergent was also inadequate for effective BOD<sub>5</sub> removal. However, the addition to wool scouring wastes of activated sludge from domestic sewage works produced a remarkably higher BOD<sub>5</sub> removal, the effluent from this process not exceeding 500 mg/ℓ<sup>120</sup>.

Since the completion of these investigations<sup>120</sup>, a modified process called the UNISAS Superactivated Sludge process<sup>238,239</sup> has been developed and investigated on a pilot scale. A pilot plant for the treatment of 6,5 m<sup>3</sup>/day of wastewater, illustrated in Fig 12, was installed at a local textile mill. It comprises an anaerobic balancing/storage tank (one day retention time), a vertical cylindrical reactor and a horizontal decanter centrifuge. Aeration is achieved by pumping the 6,5 m<sup>3</sup> of reactor contents through venturi-type air inductors placed around the periphery of the reactor and aligned to create a central vortex, to assist in the separation of air from liquid and to provide

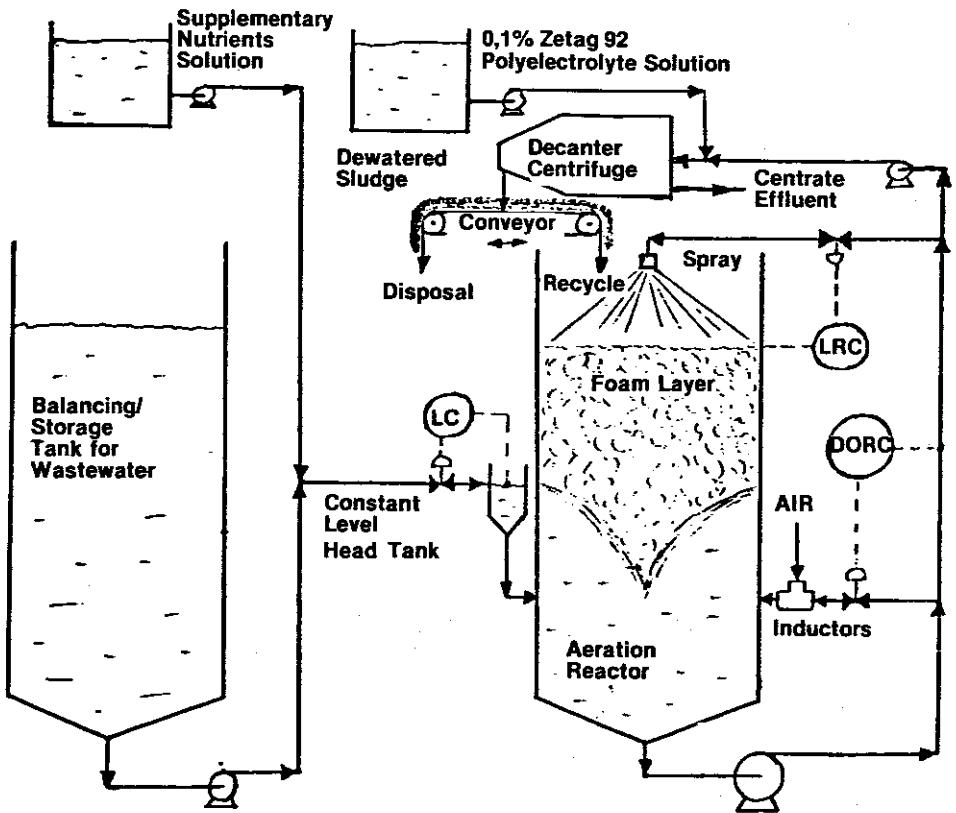


FIGURE 12

Flow diagram of the UNISAS Superactivated Sludge process<sup>238</sup>



continuity of mixing. A solution of urea and ammonium phosphate is metered directly into the contents of the reactor to provide a supplementary source of nitrogen and phosphorus nutrients based on measurements of the total organic carbon, nitrogen and phosphorus in the wastewater. A cationic polyelectrolyte is added in the feed to the decanter centrifuge to improve clarification efficiency, since the centrate is the effluent from the process unless a post-treatment facility, such as a clarifier or filter, is being used.

Automation of the pilot plant is achieved by monitoring dissolved oxygen concentration and controlling the liquid pressure to the air inductors. Furthermore, automatic control over the height of foam generated by aeration (voluminous foam production is due mainly to the high concentration of detergent used in the wool scouring process) is achieved by varying the pressure on a spray supplied from the same pump used for aeration. The concentration of suspended solids in the reactor can be controlled by discharging to waste for a predetermined portion of each hour, the dewatered sludge from the decanter centrifuge. The remaining major portion of the dewatered sludge can then be recycled directly into the reactor.

Results of pilot scale trials have shown<sup>238,239</sup> that 'shock' loading is consistently absorbed by the process without significant change in the treatment efficiency (BOD<sub>7</sub> levels in the centrate of 10 to 100 mg/l as compared with initial levels in the wastewater of 3 000 to 5 000 mg/l). It has also been shown that the size of the treatment plant required for this process is much smaller than that required for conventional biological treatments. This process has only been applied to relatively weak wastewater streams originating from the scouring, carbonising and neutralising processes<sup>239</sup>.

### **3.7.3 Anaerobic/aerobic digestion**

Aerobic treatment of wool scouring wastes involving very long treatment times ('extended aeration') has been reported<sup>227</sup>. It was claimed that complete removal of pollutants can be achieved without any sludge formation. However, this technique requires large areas of land and it has been reported<sup>95</sup> that this process has been investigated on a pilot scale at a wool scouring mill located in a rural area. The process involves settling out of heavy solids in a settling pit, a minimum of 12 days retention time in an anaerobic lagoon followed by an oxidation stage in an aerobic lagoon equipped with surface aerators and, finally, a minimum retention time of 25 days in a one-metre-deep holding pond. The process is suitable for subsequent land irrigation operations. A typical performance level of the Australian plant has been reported to be a 93% removal of biological oxygen demand<sup>95</sup>.

The principle of aerobic digestion has also been applied to the treatment of wool scouring wastes by means of the development of yet another process known as the 'Deep Shaft' process<sup>94,95,240,241</sup>. It is based on the circulation of scouring waste in a deep shaft (normally 100 metres deep) which is divided in two zones, one descendent and the other, ascendent. Air is injected at both the

beginning of the descendent zone and at the end of the ascendent zone. Part of the sludge produced by the process is recycled, very much along the lines of the activated sludge process, but no nutrients are required as in that process. A relatively long residence time is available for aerobic digestion and purified waste is continuously withdrawn from the top of the shaft. The operation of a commercial 'Deep Shaft' biological system is illustrated in Fig. 13. It has been reported that COD reductions of over 99% and volumetric reductions of the order of 75% have been achieved by means of this biological system<sup>94</sup>.

Anaerobic digestion of wool scouring wastes yields a gaseous by-product, methane, which amongst other, can be used as fuel for steam generation<sup>120</sup>. Investigations into this technique using a four stage digester unit, maintained at 37 to 38°C, indicated that the rate of methane gas production achieved with

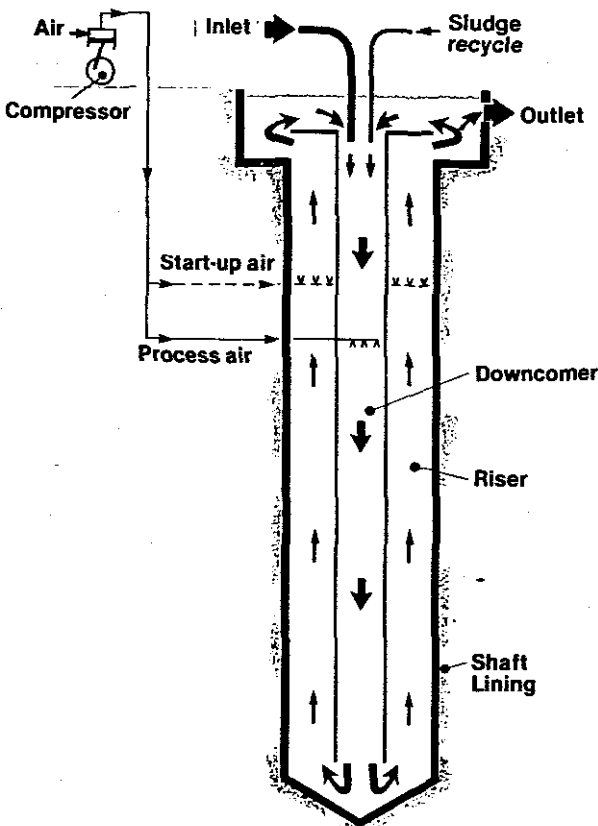


FIGURE 13

Schematic representation of a commercial 'Deep Shaft' biological system<sup>94</sup>

domestic sewage was not significantly affected by the introduction of wool scouring sludge originating from acid cracking (see Section 3.1). Experiments involving the addition of enzymes to accelerate biological activity were also performed.

### **3.7.4 Land irrigation**

This technique has been reported<sup>227</sup> to be simple and effective when a large land area is available for this operation (required area has been estimated at about 5 hectares for every 1 000 kg/h greasy wool input to the scour). Wool scouring wastes contain certain amounts of nitrogen and potassium which could serve as a cheap source of food for vegetation and in dry climates their water content alone may be of considerable value<sup>227</sup>. However, in practice, there are some problems arising from the use of this technique for the disposal of wool scouring wastes i.e. blocking of pipelines by suspended solids and grease and gradual accumulation of grease and suint salts in the soil<sup>227</sup>.

To solve the first problem a preliminary settling stage for these wastes followed by sludge drying and disposal on land would be a definite necessity<sup>227</sup>, whereas to solve the second problem i.e. slow biological degradation of wool grease, a series of preliminary treatments were found to be required. These included long anaerobic treatment in a lagoon, followed by a shorter aerobic treatment and followed by another very long treatment in a final lagoon, from which the liquor is pumped to the irrigation area<sup>227</sup>.

This technique has been reported to be, in general, relatively cheap for scouring mills in a rural location where cost of land is low. However, problems related to long-term operation of the process have not as yet been resolved. In certain cases, incorporation of anaerobic/aerobic treatments prior to spraying would seem recommendable. Finally, the effect of accumulation of sodium on the soil structure has been studied for the last four to five years but final conclusions have not been reached at this stage.

### **3.8 Evaporation and Incineration**

This two-stage technique for treatment of wool scouring wastes has been mainly used in the last decade or so in Japan. During the evaporation stage, water is physically separated from all the contaminants. Evaporation can be partial or complete. Evaporation to dryness has been reported<sup>227</sup> not to be a practical proposition except by spray or freeze drying, which are known to be too expensive. As soon as the residues become fairly concentrated, many difficulties occur in liquor handling and heat transfer<sup>227</sup>. Therefore, in practice, evaporation has been confined to the removal of about two-thirds of the water as a preliminary stage to incineration.

Re-use of the distilled water obtained by evaporation has been reported<sup>227</sup> not always to be possible because it contains significant quantities of volatile organic compounds. It constitutes, however, a relatively unpolluted stream which complies with the requirements of municipal authorities for discharge in the sewer and it can, in general, be re-used for numerous purposes.

The evaporation stage can be replaced by ultrafiltration which would allow, in practice, removal of more than 90% of the water<sup>227</sup>. This alternative technique for purification of wool scouring wastes is discussed in the next section.

Evaporation of wool scouring wastes using *natural evaporation* has been investigated by SAWTRI<sup>242</sup>. Experiments carried out on different, specially prepared wool scouring wastes, showed that the efficiency of evaporation tended to be approximately proportional to the percentage of surface area of waste not covered by grease. The latter, however, was not necessarily proportional to the amount of grease in the waste but could depend also on emulsion stability<sup>242</sup>.

In Japan, the evaporation and incineration process used for the disposal of wool scouring wastes has been reported<sup>243</sup> to comprise multi-stage flash evaporation combined with incineration in a furnace. The process produces an effluent with a BOD of less than 50 mg/l and a suspended solids content of less than 10 mg/l.

Incineration of the concentrate produced during the previous evaporation step has been reported<sup>243</sup> to be carried out in various types of furnaces, mostly of the multiple hearth and fluidized bed type. These operate in the temperature

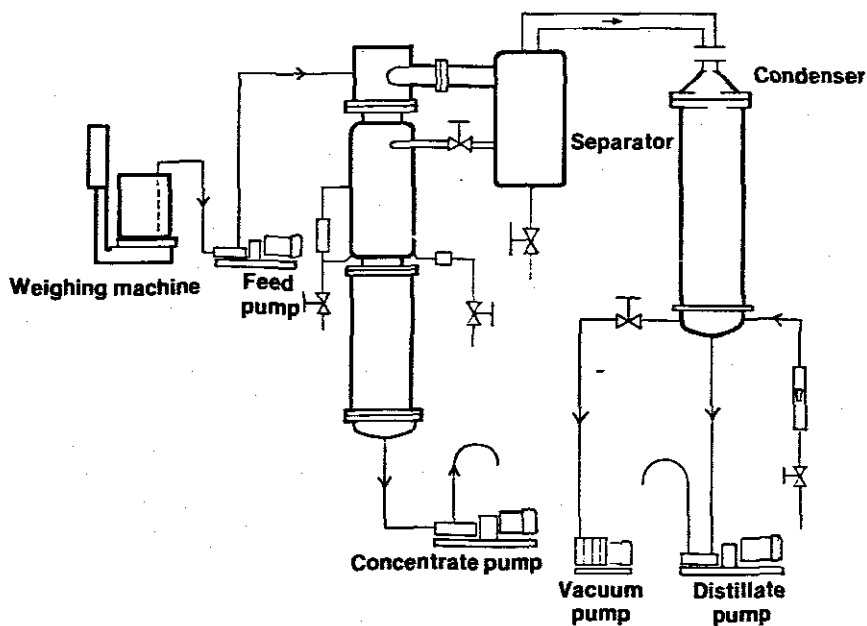


FIGURE 14  
Schematic representation of a scraped film evaporator<sup>94</sup>

range of 1 000 to 1 400°C and produce an ash with a high melting point. This ash can cause serious problems due to its high potassium content (derived from the suint) which attacks the refractory materials of the furnace. It has been suggested<sup>243</sup>, however, that this effect could be avoided by operating the furnace at lower temperatures e.g. below 800°C.

New developments in the field of evaporation/incineration have been recently reported<sup>143</sup>. Evaporation of wool scouring wastes was investigated in two types of evaporators i.e. a scraped film evaporator and a plate evaporator. Incineration of the final concentrate from evaporation was investigated in a specially designed incinerator<sup>94</sup>.

Research into the performance of the scraped film evaporator (see Fig. 14) showed that it works well in this kind of application. It was found in practice that concentration factors for total solids content (TS) of the order of six were fairly typical, the TS content of these wastes normally being increased from about 6 to 35%. The distillate was of good quality and had a residual COD level of 450 mg/l. Average steam consumption was found to be 1 kg steam/kg feed<sup>94</sup>.

Very good results were reported for evaporation of wool scouring wastes in plate evaporators in series (see Fig. 15). Concentration factors in terms of total solids content of as high as seven were obtained, the average steam consumption being of the order of 1,05 kg steam/kg feed<sup>94</sup>.

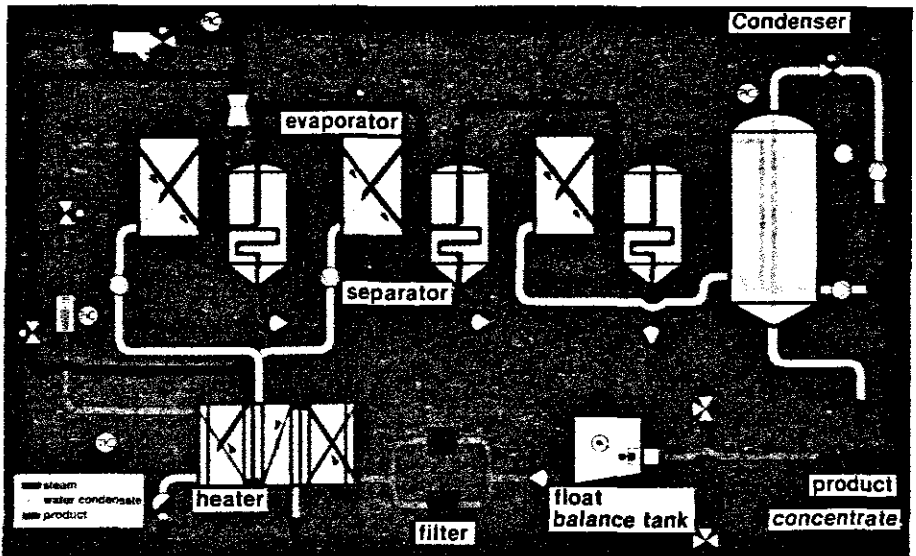


FIGURE 15  
Flow diagram of a 3-stage plate-evaporation plant<sup>94</sup>

Incineration trials were carried out in an incinerator which uses natural gas as auxiliary fuel burner and which has as a special feature a quench vessel for the removal of salt (see Fig. 16). Wool scouring wastes were pumped through a series of fluid atomising jets, steam or compressed air being used as atomising fluid.

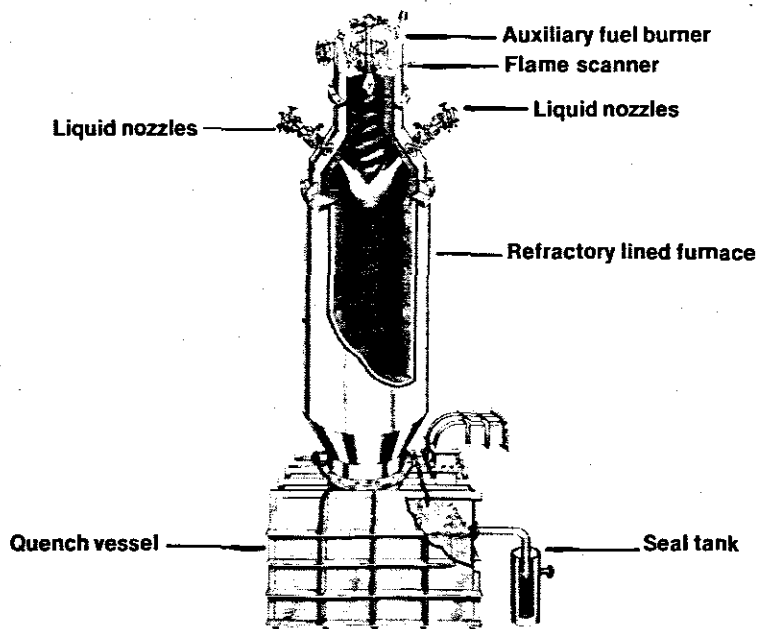


FIGURE 16

Schematic representation of a specially designed incinerator equipped with gas quench system<sup>94</sup>

It was found<sup>94</sup> that minimum total solids contents of 35 to 40% in the feed to the incinerator were required to ensure that the process was economically viable. Typical conditions in the incinerator were a temperature of 800°C and an adjustment to the ratios of gas to air to give 4% excess oxygen. In general, the evaporation/incineration process described previously was found<sup>94</sup> to be efficient but costly.

Two more studies<sup>244,245</sup> on treatment of wool scouring liquors by evaporation have been published in the last two years. The first of these<sup>244</sup> has shown that such a process can produce a sludge which solidifies on cooling and it probably would allow the wool scourer to use the sewer only for discharge of rinse water produced during the scouring operation. However, the evaporation process would only become economical if the latent heat of the steam

produced would be used to advantage in the scouring plant or elsewhere in the textile mill and the volume of scouring liquor requiring treatment would not exceed one litre per kg of greasy wool scoured<sup>244</sup>. The second study<sup>245</sup> dealt with the use of a scraped film evaporator for partial treatment of wool scouring liquors. The steam to evaporation ratio was found to be 1,2 to 1,5 kg/kg and the evaporation rate 100 to 125 kg/m<sup>2</sup>/hr. A spadeable sludge was produced (total solids content of up to 58%). It was found, however, that the carbon-graphite rotor blades wore at such a rate that use of harder wearing materials was recommended for possible commercial application of this technique<sup>245</sup>.

### 3.9 Membrane Separation

Two similar membrane separation techniques i.e. ultrafiltration and microfiltration have been investigated for the treatment of wool scouring wastes and, particularly, wool scouring effluents originating from centrifuging of liquors (these represent the weaker polluted streams in the scouring industry not considering rinse waters). Both techniques are used for separating high molecular weight solutes or colloids from polluted streams. The feed solutions are made to flow under pressure past the membrane, and the rejected solutes leave with the flowing stream. The continuous flow ensures a self-cleaning effect of the membrane and the permeate (ultrafiltrate or microfiltrate) can be collected in a shell or a suitable receptacle. The basic difference between both techniques is the average pore size of the membrane used for the separation process, the former being typically 0,005  $\mu\text{m}$  and the latter 2  $\mu\text{m}$ . The variation in average pore size is accompanied by a variation in pressure levels required for the filtration process.

#### 3.9.1 Ultrafiltration

This separation technique has been applied to wool scouring effluents<sup>164,247-256</sup> with the purpose of producing an ultrafiltrate of a quality suitable for disposal into the sewer. Usually wool scouring liquors are centrifuged to remove some of the grease and coarse suspended solids before entering the ultrafiltration plant. Blinding of the membrane has been found to be one of the major problems associated with ultrafiltration. Regeneration of the membrane has been achieved to a large extent by proper backwashing. The decay in ultrafiltrate flux rate has been studied thoroughly. Variables such as type of membrane, nominal molecular weight cutoff, time, feed concentration, pressure differential, pH and temperature of the feed have all been found to affect the ultrafiltrate flux rate.

Four different types of ultrafiltration membranes have been studied until now for treatment of wool scouring liquors, namely Abcor, Dorr-Oliver, Berghof and Romicon. The first type consists of a thin membrane film, such as cellulose acetate, which has been placed onto a glass-fibre resin-reinforced and porous tubular support<sup>247</sup>. The second type consists of a plate and frame module comprising planar filter leaves mounted on a plastic base and is

reported to be a copolymer of polyvinyl chloride and acrylonitrile<sup>251</sup>. The third type consists of a thin polytetrafluoroethylene membrane film placed on a highly porous asymmetrical support medium<sup>252</sup>. The fourth type consists of hollow tubes potted at both ends of a clean polysulphone shell<sup>254</sup>. Pressure conditions for these membranes varied between approximately 25 and 350 kPa. The nominal molecular weight cutoff of these membranes varied approximately between 25 000 and 100 000 (roughly equivalent to pore sizes of 0,004 to 0,011  $\mu\text{m}$ ).

It was claimed<sup>247</sup> that wool grease from the membrane concentrate fraction could be economically recovered and that the aqueous ultrafiltrate fraction could be successfully re-used or be disposed of by treating wool scouring liquors (or the effluent phase after centrifuging) in an Abcor ultrafiltration plant. However, no evidence of industrial application has been found in the literature. On the other hand, studies carried out on a Dorr-Oliver ultrafiltration plant<sup>164,248,249</sup> showed encouraging results. Ultrafiltrate fluxes were shown to be very dependent on experimental time and feed concentration. Recycling at zero pressure differential, however, resulted in almost a complete flux regeneration and a clear solution (of up to 85% of the original volume) was achieved at a low estimated operation cost<sup>249</sup>.

Studies carried out on a Berghof ultrafiltration plant<sup>250</sup> showed that ultrafiltrate flux rate was dependent on the grease and total solids content of the feed solution. Ultrafiltrates with an average residual grease content of only 300 mg/l were obtained<sup>250</sup>. In general, rejection factors for grease and suspended solids were very high, with values close to 95% for the former and close to 100% for the latter. Ultrafiltrate flux rates of 20 to 120  $\ell/\text{m}^2/\text{hr}$  were obtained for total solids contents of the feed in the range of 5 to 20%.

Pilot studies carried out at SAWTRI on a Romicon ultrafiltration plant<sup>254</sup> showed results similar to those reported with the Dorr-Oliver system<sup>248,249</sup>. Ultrafiltrate flux rates fluctuated between 20 and 95  $\ell/\text{m}^2/\text{hr}$  for total solids contents of the feed varying from 5 to 20%. Ultrafiltrate with an average residual grease content of 300 mg/l and rejection factors for grease and total solids of up to 99 and 93%, respectively, were reported<sup>254</sup>.

Results of another study<sup>255</sup> showed that the Romicon system compared favourably with the Abcor system as far as economics was concerned. Some susceptibility to blockage of the former membrane was reported<sup>255</sup>.

A more recent study on ultrafiltration with a Iopor membrane-type Dorr-Oliver plant<sup>256</sup> has clearly proven the feasibility of this technique for producing a permeate completely free from suspended solids and grease, together with a concentrated sludge from a strong wool scouring effluent at a moderate cost. The process appeared to be particularly applicable for areas where there are stringent effluent standards.



As an effluent purification technique, ultrafiltration provides an initial reduction in the pollution load by concentrating grease and suspended solids into a concentrate but this concentrate creates its own effluent problem. Possible means of destabilising this concentrate, however, were discussed in Section 3.4. The ultrafiltrate which contains almost entirely suint can, however, be partially recycled to the scouring bowls<sup>257,258</sup>, thus reducing fresh-water usage. From an economic point of view it has been reported<sup>255</sup>, that in order to be viable, ultrafiltration membranes ought to offer a useful life of at least two years. However, extended operating tests to the point of failure, under rigorously controlled temperature and pressure conditions, are still required for an estimate of the life of these ultrafiltration systems in general to be evaluated for wool scouring effluents.

Problems associated with ultrafiltration systems in general are reported<sup>262</sup> to be, amongst others, the excessive blockage of the membrane (which would necessitate some kind of pre-filtration stage), temperature and pressure limitations and cleaning procedure for the restoration of the flux rate. These problems occurred in spite of the good grease and suspended solids rejection performance showed by the membrane initially<sup>250,259</sup>. To overcome some of the problems of the classical ultrafiltration technique, the dynamic membrane ultrafiltration technique has lately been developed<sup>260</sup> and used for the purification of wool scouring effluents.

Dynamic membrane ultrafiltration was investigated<sup>261</sup> on a pilot scale, the pilot plant (Fig. 17) consisting of modules containing each a number of porous stainless steel tubes, on which a chemical membrane of the zirconium or zirconium/silicate type was formed.

It was found<sup>261</sup> that membrane flux rate could be maintained at a relatively high value for 10 to 14 days, after which detergent cleaning allowed successful restoration of the initial flux rate performance. Permeate flux rates of 80 to 90  $\text{l/m}^2/\text{hr}$  and rejection factors for grease and suspended solids of 100% were obtained. The permeate was found to be suitable for recycling to the scour. Among the disadvantages of this ultrafiltration technique, however, are the high costs for porous stainless steel tubes and high pressure requirements e.g. of the order of 2 to 3 MPa<sup>261</sup>.

### 3.9.2 Microfiltration

A laboratory scale study of the particle size distribution of suspended solid dirt in wool, mohair and karakul scouring wastes was carried out at SAWTRI<sup>50</sup> with a view to ascertain the approximate pore size which would be theoretically required for an efficient removal of this contaminant. The results of this study indicated that efficient removal of suspended solids from the effluents produced by centrifuging of liquors could be expected by microfiltration of such liquors through pores which are relatively coarse (0,1 to 10  $\mu\text{m}$ ) by ultrafiltration standards. In fact, theoretically, an average of 95% rejection of the suspended solids was obtained by using a filter with a pore size of 0,5  $\mu\text{m}$ <sup>50</sup>.

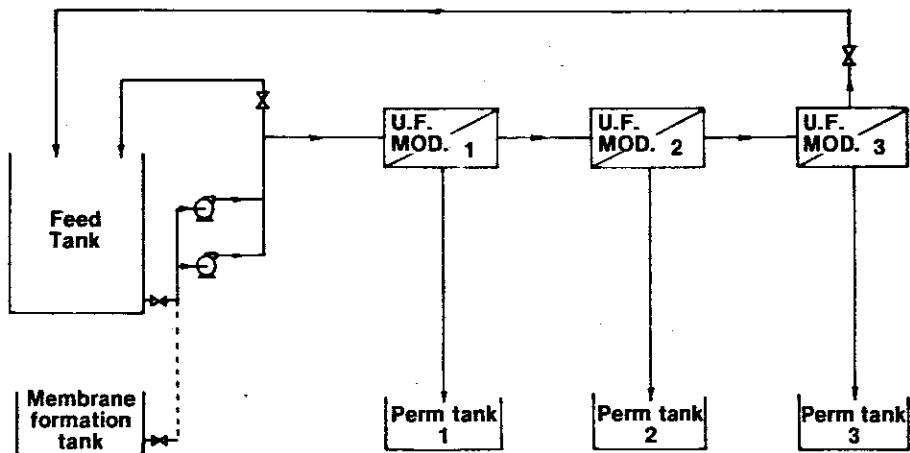


FIGURE 17

Schematic flow diagram of a dynamic membrane ultrafiltration unit<sup>262</sup>

Laboratory and pilot studies carried out at SAWTRI<sup>263,264</sup> showed that microfiltration of wool scouring effluents through long porous nylon tubes with an average pore size of  $2\ \mu\text{m}$  (a pore size about 400 times greater than that found typically in ultrafiltration practices) is feasible. It was found that an inlet pressure of 500 kPa and a backpressure of 250 kPa gave a good quality microfiltrate (0,05% residual grease and 0,03% suspended solids). A 24% decay in permeate flux rate was obtained during 6 hours operation of the plant, the average flux rate being about  $10\ \ell/\text{m}^2/\text{hr}$ <sup>264</sup>. Although the life expectancy of the nylon tubes investigated is unknown at present, the idea of microfiltration using tubes with an average pore size of  $2\ \mu\text{m}$  is certainly interesting because it opens this technique to a wide range of porous materials of various kinds.

It is hoped that future research into porous media will allow the development of highly resistant tubes with a pore size in the suitable range (1 to  $3\ \mu\text{m}$ ).

#### 4. ECONOMICS OF MODERN PROCESSES FOR TREATMENT OF WASTES

Limited information on this topic has been made available by various research centres around the world. However, during the three years, 1979 to 1981, a number of economical assessments have been published<sup>194,95,134,204,205,238,239</sup>. The main difficulty in interpreting the findings of these feasibility studies is that comparisons become difficult as a result of inflation and fluctuations in exchange rates. To overcome this problem, the

author has decided to adjust all published information in accordance to the annual inflation rates of the country of its publication. This resulted in economical data being obtained for the various modern processes as at the end of 1981, current exchange rates being used to express all amounts in one currency. Values for annual inflation rates used for this purpose are summarised in Table 7. The exchange rates used were in accordance with those prevailing during December 1981, as follows:

1 £ = R1,91 and 1 \$ Aust. = R1,12.

**TABLE 7**  
**ANNUAL INFLATION RATES(%) USED IN THIS SURVEY**

COUNTRY	1979	1980	1981
South Africa	13,1	13,8	15,5
United Kingdom	13,4	18,0	12,4
Australia	9,1	10,2	10,5

The general state of affairs as far as the economics of most of the modern processes is concerned is reflected in Tables 8, 9 and 10. Tables 8 and 9 are based on information supplied by the IWS<sup>94,95</sup> and Table 10 on information supplied by various research centres at the 6th International Wool Textile Research Conference, held in Pretoria, South Africa in 1980<sup>134,205,239</sup>. The information given in Table 9 is based on a WRONZ scouring system processing 4 500 tonnes of greasy wool per annum (64's quality), plant amortised over 5 years at 15% interest and effluent treated to river quality by normal sewage works. The information given in Tables 8 and 10 is based on a classical scouring train capable of scouring 5 000 tonnes of greasy wool per annum (64's quality) at a liquor ratio of 10 l/kg greasy wool and again, plant amortised over 5 years at 15% interest.

On the whole, the data supplied in Tables 8 and 10 are by no means conclusive, although some clear trends can be observed. It is quite obvious that the UNISAS Superactivated Sludge process appears to be relatively cheap (Table 10) but since no data has been reported on additional costs for sludge disposal\*, it is difficult to decide whether this process stands in a clearly advantageous position in respect of other processes such as the CSIRO Lo-Flo process and the SAWTRI BITFLOC process (which showed total costs of approximately R41 and R43 — R48 per tonne of greasy wool, respectively). In

\*Solid sludge disposal has been reported to be expensive, particularly in the UK<sup>94</sup> where it can reach R16 per tonne.

general, all other processes whose economics were available showed higher costs (particularly when compared to the cost of effluent discharge into the drain i.e. about R50/tonne greasy wool).

**TABLE 8**  
**EFFICIENCY AND ECONOMICS\* OF A FEW MODERN PROCESSES**  
**FOR TREATMENT OF WASTES, BASED ON A 1980 PUBLICATION BY**  
**THE IWS<sup>95</sup>**

Type of Process	Method/Equipment	%COD Reduction Expected	Approx. Capital Cost (R)	Comments
Centrifugal separation and evaporation	ITF/Alfa Laval or Dewavrin centrifugal removal of grease followed by evaporation	100	1 110 000	Expensive in capital and energy costs
Acid cracking	(a) Traditional. Tanks for cracking and settling — magma boiler filter pressing to give grease	80-85	200 000	Labour intensive. High in chemical cost but some income can be obtained from acid cracked grease
	(b) UNSW Hot Acid Process. Continuous acid cracking at pH 2.5 - 3.0 in reactor followed by neutralisation, flocculation and sedimentation and continuous sludge dewatering via decanter centrifuge	85	260 000	Efficient and rapid emulsion cracking giving high solids sludge disposal to land.
Chemical Flocculation	(a) Traflow W. Ferrous sulphate/lime/filter aid coagulation — rotary vacuum filter	85-95	210 000	Expensive in filter aid
	(b) Flocculation with alum, ferric chloride or calcium chloride preferably with polyelectrolyte. Settling, sludge dewatering via rotary vacuum filter or decanter centrifuge	85-90	210 000	Expensive if filter aid used but less so if decanter centrifuge is used.
	(c) WRONZ rationalised scouring and effluent treatment process	47	190 000	Low capital cost but requires some further effluent treatment process for reasonable COD reduction.
	(d) WRONZ Mini-bowl scouring and effluent treatment process	59	150 000	Very low capital cost but still requiring some further effluent treatment process
	(e) Mini-Flo process	65	560 000	High capital cost and requires some further effluent treatment process.
	(f) Modified Mini-Flo process, including evaporator	92	680 000	High capital cost but improved effluent treatment ability and grease recovery
	(g) SAWTRI BITFLOC process. Flocculation with 5% (v/v) bitterns or 1% (m/v) magnesium chloride followed by sludge dewatering in a decanter centrifuge	95	210 000	Potential low cost process if plant is near to sea (bitterns can be used as flocculant), otherwise slightly more expensive (magnesium chloride is required).
Alcohol Destabilisation	DSIR Alcohol Destabilisation process. Uses n-pentanol to crack emulsion to give top grease phase, middle suint phase and bottom dirt phase which are separated by steam distillation columns.	75	360 000	Fairly expensive in both capital and running costs
Biological Treatment	(a) Settling followed by anaerobic lagoon, aerobic lagoon and final dilution pond-land irrigation.	97	320 000	Cheap process where land is available, running costs are low.
	(b) ICI Deep Shaft. Effluent passes down a 'Deep Shaft' with air/oxygen injection in downcomer giving rapid oxygen transfer and rapid biological degradation.	99,7	660 000	Expensive in capital cost but low in running cost
	(c) UNISAS Superactivated Sludge process. High rate activated sludge process at elevated temperature.	98-99	210 000	Low in capital costs and running costs.
Ultrafiltration and Evaporation	Dorr-Oliver IOPOR ultrafiltration followed by evaporation of concentrated phase	80-85	530 000	High costs in membrane replacement and expensive in running costs.
Evaporation and Incineration	Evaporation of scour liquor to 30-40% total solids, sludge drying and incineration	100	790 000	Expensive in capital and energy costs

\*Adjusted for inflation.

**TABLE 9**  
**ECONOMICS\* OF A FEW MODERN PROCESSES FOR TREATMENT**  
**OF WASTES, BASED ON A 1979 PUBLICATION BY THE IWS<sup>94</sup>**

Process	Capital Cost of Treatment Plant (R)	Annual Running Cost (R)	TOTAL COST (R/Tonne greasy wool)
Continuous Acid Cracking with centrifugal sludge dewatering	300 000	142 600	56,48
Ultrafiltration/Evaporation	490 000	147 700	65,15
Evaporation/Incineration	750 000	351 400	127,61
ICI 'Deep Shaft' biological treatment without sludge disposal	650 000	74 200	60,04
ICI 'Deep Shaft' biological treatment with disposal of sludge by tanker	650 000	254 900	100,20
Lo-Flo	350 000	81 900	41,05
No treatment — effluent discharged to drain	—	224 100	49,81

\*Adjusted for inflation

From the processes whose economics in terms of running costs have not been assessed yet, the IWS Mini-Flo process is reported<sup>95</sup> to hold some promise, in spite of the high capital costs which it entails.

Finally, not all the processes dealt with in Table 8 produce the same extent of purification. The efficiency of the various processes, expressed in terms of % COD reduction expected, can be seen to be very good (95 to 100%) for only a selected number of processes i.e. ITF/Alfa Laval, SAWTRI BITFLOC, anaerobic/aerobic biological treatment, ICI 'Deep Shaft', UNISAS Superactivated Sludge and evaporation/incineration. As discussed before, from these processes the available economical data (Tables 8 to 10) would tend to indicate that processes such as the UNISAS Superactivated Sludge, the CSIRO Lo-Flo and the SAWTRI BITFLOC are among the most economically viable at present.

**TABLE 10**

**ECONOMICS\* OF A FEW MODERN PROCESSES FOR TREATMENT OF WASTES BASED ON A NUMBER OF PAPERS DELIVERED AT THE 6TH INTERNATIONAL WOOL TEXTILE RESEARCH CONFERENCE HELD IN 1980 IN PRETORIA** 134, 205, 239

Process	Alternative Scheme used	Capital Cost of Treatment plant (R)	Annual running cost (R)	TOTAL COST (R/Tonne greasy wool)
UNSW Hot-Acid Flocculation, Neutralisation and continuous sludge dewatering via decanter centrifuge	No recycle of treated effluent	395 000	174 700	58,51
	50% recycle of treated effluent	395 000	160 200	55,61
UNISAS Super-activated Sludge process without sludge disposal	No recycle of treated effluent (sewer quality)	195 000	38 400	19,32
	50% recycle of treated effluent (river quality)	240 000	27 900	19,90
Treatment of sludge streams by means of the SAWTRI BITFLOC process and solid sludge disposal on land	Using Bitterns as Flocculant (if factory is close to a common-salt recovery plant)	215 000	151 300	43,09
	Using MgCl <sub>2</sub> flakes as flocculant (if factory is located in-land)	215 000	177 800	48,39

\*Adjusted for inflation.

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