

**A PROCESS FOR THE DETANNING OF
CHROME LEATHER WASTES UTILISING
TANNERY EFFLUENTS**

THESIS

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ABBREVIATIONS AND SYMBOLS

~	= approximately
APHA	= American Public Health Association
AWWA	= American Water Works Association
COD	= chemical oxygen demand
conc	= concentration
Cr	= chromium
Cr ³⁺	= trivalent chromium
Cr ⁶⁺	= hexavalent chromium
DNA	= Deoxyribonucleic acid
FAS	= ferrous ammonium sulphate
JALCA	= Journal of the American Leather Chemists' Association
JSLTC	= Journal of the Society of Leather Trades' and Chemists
Liri	= Leather Industries Research Institute
M	= molar
mS.m ⁻¹	= milliSiemens per metre
N	= normal
pH	= negative logarithm of the hydrogen ion concentration
PV	= permanganate value
rpm	= revolutions per minute
TKN	= total kjeldahl nitrogen
WPCF	= Water Pollution Control Federation
w/w	= weight/weight

Chemical formulae not included in this list are defined in the text.

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For my parents.

ABSTRACT

The considerable volume of chromium-bearing wastes generated during the process of leather tanning, exacerbated by the potential for trivalent chromium in the wastes to be oxidised to the toxic hexavalent state, has created a major waste disposal dilemma for the tanning industry. While methods are available for the safe and effective treatment of residual chrome-tanning liquors, little has been done to address the issue of the chrome-bearing solid wastes. Given the increasingly stringent environmental compliance standards facing tanneries, unless an appropriate treatment process is developed in the immediate future, the continued use of chromium as a tanning agent could be compromised.

Recent investigations have demonstrated the potential of heated alkaline conditions for dechroming these solid wastes. This study expanded upon these considerations and examined the feasibility of utilising the highly alkaline tannery waste effluents as cost-effective, substitute alkaline media. The three effluents considered in this study, classed as lime sulphide liquors, were shown to be capable of dechroming wet blue shavings, with resultant separation of the solid wastes into a protein and a concentrated chromium product. The solubilised protein product contained low chromium concentrations which comply with legal discharge limits. The precipitated chromium product offers opportunity for reutilisation in the tannery. A novel industrial-scale treatment process, based on these investigations, indicated the process to be capable of treating the quantity of shavings produced on a daily basis by a medium to large scale tannery. Application of this method for the dechroming of other chrome-tanned solid wastes was also shown to be feasible.

CHAPTER 1

INTRODUCTION

The introduction of chromium as a tanning agent in the late 19th century revolutionised the process of leather manufacture (Siegler, 1987). Previous tanning methods were frequently time consuming and did not always produce leather of a high quality (Thomson, 1985). The introduction of chromium as a tanning agent made available a tanning process that was rapid, easy to use and cost-effective. Yet, the most outstanding feature of chromium tanning was that it produced high quality leather, far superior to that attainable with any previous tanning agent (Gauglhofer, 1990). Consequently, chromium generally replaced other tanning agents and became established as the standard tanning process throughout the world (Elsinger, 1988). The discovery and early use of chromium chemicals in leather manufacture is the subject of a detailed review by Thomson (1985).

Chromium, like other tanning agents, stabilises the collagen protein of hides and skins by forming cross-linkages between the polypeptide chains (Langerwerf, 1985). This process affords the collagen fibres greater mechanical strength (Meyer, 1942) and renders the final leather product resistant to microbial decay (Lollar, 1958). It is now known that chromium tanning involves the formation of co-ordinate covalent bonds between the chrome tanning salts and the protein side chain carboxyl groups (Thorstensen, 1993). These bonds differ from conventional covalent bonds in that both electrons are donated by only one of the bonded atoms, as opposed to conventional covalent bonds where each atom furnishes one electron to the bond pair. Co-ordinate covalent bonds are therefore weaker and more polar than covalent bonds (Thorstensen, 1958). Shuttleworth (1958) and Thorstensen (1993) have dealt in detail with the different bonding processes involved in chromium tanning. The essential stages in the manufacture of a chrome-tanned hide and the principal chrome-bearing wastes produced are outlined in Figure 1.1.

Despite its many advantages, chromium tanning has in recent years also attracted increasing attention of an adverse nature. This is mainly as a result of the chemical characteristics of chromium compounds (Lollar, 1986) and their associated effect on the environment, including Man himself (Gauglhofer, 1986). Chromium is a heavy metal and is, in consequence, considered to be an environmental pollutant. Furthermore, some chromium compounds have been shown to be toxic and even carcinogenic (Gauglhofer, 1990).

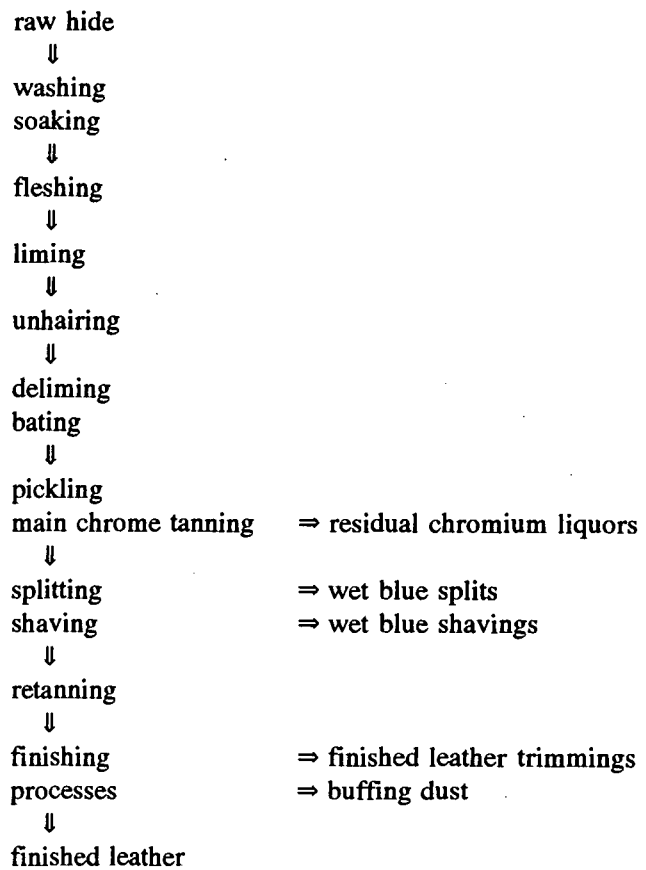


Figure 1.1. Flow diagram of the classic chromium tanning process showing the origins of the principal chromium-containing wastes generated.

The degree of toxicity of chromium is a function of its oxidation state (Bataille *et al*, 1983). Chromium can assume all oxidation states from -2 to $+6$, of which only two are environmentally stable, viz. trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}) (Hartford, 1979; Snow and Xu, 1991). The chromium used in the tanning process is added as basic chromium sulphate, where it is present in the trivalent state (Menden and Rutland, 1988). Trivalent chromium compounds are normally characterised by very low bio-toxicity, mainly due to their restricted ability to traverse biological membranes (Anttila, 1990). However, the potential, although remote, does exist for trivalent chromium to become oxidised under natural conditions to the hexavalent state (Bauer *et al*, 1977), in a reaction which is reversible (Shivas, 1980). Hexavalent chromium compounds can cross biological membranes (Beyersman *et al*, 1984) and are toxic, in low concentration, to both plant and animal life (Shivas, 1978). Baruthio (1992) has reviewed the adverse health effects of chromium and its compounds.

The potential toxicity of chromium has prompted legislation specific to the tanning industry in an attempt to restrict the discharge of chromium to the environment in forms other than the finished product (Gauglhofer, 1990). In many instances this legislation has tended to be unnecessarily restrictive, often more focused on hexavalent, rather than trivalent chromium toxicity (Patton and Ellison, 1977). This was instituted largely as a precaution against the theoretical possibility of disposed trivalent chromium being oxidised to the toxic hexavalent state (Darrie, 1991). This has, however, resulted in a waste disposal problem for the tanning industry, which is finding it increasingly difficult to comply with these stringent regulations (Kochta *et al*, 1990). In some cases, for example where the conditions and expenses involved have not been sustainable, tanneries have even been compelled to close (Alexander *et al*, 1992). The tanning industry have argued that the regulation of tannery waste should be consistent with the environmental risks associated with trivalent chromium, given that trivalent chromium should be the only form of chromium present in the wastes discharged (Patton and Ellison, 1977).

However, recent evidence concerning the mutagenicity of chromium has indicated that trivalent chromium may be more toxic than originally believed. Although early mutagenic assays usually confirmed the non-toxic nature of trivalent chromium and the potent mutagenic properties of chromium in the hexavalent state (Gaur and Bhattacharjee, 1991; Gao *et al*, 1992), recent evidence has shown that it is, in fact, salts of the trivalent state that are the ultimate Deoxyribonucleic acid (DNA) damaging compounds. They have been shown to induce DNA-protein and DNA-DNA cross-linking, while the Cr^{6+} salts induce single strand breaks in DNA (Bianchi *et al*, 1983). The non-toxic behaviour of trivalent chromium salts is now attributed more to the restricted ability of these salts to cross plasma membranes, rather than to the specific oxidation state itself (Connett and Wetterhahn, 1983). The same authors have proposed an uptake-reduction model to explain the carcinogenic activity of chromium. In this model the hexavalent chromium species is transported across the plasma membrane and once in the cellular fluids and tissues, is rapidly reduced to substitutionally inert chrome III complexes, which then exert a mutagenic effect. Since the genotoxic effects of Cr^{3+} become apparent at extremely low concentrations, the uptake of small quantities of Cr^{6+} , possibly originating from oxidation of Cr^{3+} in tannery waste, now becomes significant (Snow and Xu, 1991). This recent evidence is now refuting the validity of the tanning industries' earlier opposition to the application of stringent disposal regulations and it is clear that action is required to address the adequate disposal of chrome-bearing tannery wastes. Two principal options are therefore open to the industry: either the tanning process must be altered to eliminate or alleviate the chromium problem, or the chrome-bearing waste produced must be effectively addressed.

An obvious solution would be to consider the use of alternative tanning agents, as this would eliminate the problem of chromium altogether in the wastewaters and solid wastes produced. Extensive investigations into the viability of alternative tanning agents have been undertaken (Siegler, 1987; IULTCS Congress Report, 1990). Kochta *et al* (1990) have reviewed current alternatives to chrome tanning and the *status quo* on complete or partial substitution of chromium compounds by vegetable tanning materials, alternative mineral salts, and reactive organic compounds is discussed. Both Kochta *et al* (1990) and Darrie (1991) have compared selected properties of these alternative tanning agents to chromium. The general consensus of all these studies is that while some tanning agents appear to be more ecotoxicologically acceptable than chromium, others are of even higher toxicity than Cr⁶⁺. It must, however, be borne in mind that it is unlikely that the toxicological properties of those tanning agents which presently appear less toxic have been studied in as much detail as chromium, and they may yet prove to be even more toxic (Darrie, 1991). The mutagenic properties of alternative tanning agents must be considered suspect by virtue of their very action, since the ability of any tanning agent to stabilise the anionic trihelix of collagen automatically implies that it could possibly also interact with the anionic double helix of DNA (Langerwerf, 1985). Furthermore, public demand for the qualities of chrome-tanned leather invalidates any ecotoxicological advantages of alternative tanning agents, but at the same time, also exacerbates the chrome-waste disposal problems (Leather, 1984).

A second possible approach could involve modification of the tanning process to reduce the discharge of chromium to the environment (Gauglhofer, 1990). In the conventional tanning process approximately 40%, or more, of the chrome tanning agent remains unused in the residual tanning liquor and is discharged from the tannery (Langerwerf, 1985). Modifications involving innovations such as optimisation of chromium fixation (Covington *et al*, 1983), dry tanning or "no float" processes (Gauglhofer, 1990), and direct injection of the tanning liquor into the hide (Leather, 1991), amongst others, leads to a significant reduction in the amount of chromium discharged in the tannery effluents. However, it is considered unlikely that these methods alone will enable tanneries to comply with the anticipated stringency of future legislation (Darrie, 1991). The inability of such processes to address the solid wastes at the same time underlines the pressing need for a reliable and comprehensive treatment process, and one which will keep a step ahead of the increasingly stringent disposal regulations.

Although the greatest discharge of chromium from the tannery occurs in the form of the residual liquors discharged from the chrome tanning baths (Langerwerf, 1985), successful treatment methods have been developed for these wastewaters, in many cases with concurrent recovery and reuse of the chromium in the tannery. Treatment principally involves precipitation of the

chromium with an alkaline reagent, followed by filtration, and dissolution of the filter cake in an acid medium to provide a chromium stock for reutilisation (Collivignarelli and Barducci, 1984; Tsotsos, 1986). Conversely, the treatment and disposal of the solid wastes remains a major problem.

Chrome-bearing solid wastes are generated at several stages in the tanning process (Figure 1.1), with wet blue shavings, wet blue splits and finished leather trimmings constituting the bulk of the solid chrome wastes (Vulliermet, 1980). The generation of these three categories of solid waste is outlined very briefly in Chapter 2. As will be discussed below, attempts have been made to treat these wastes (Taylor *et al*, 1990; Alves dos Reis and Beleza, 1991a), but it would appear that no adequate process has yet been implemented on an industrial scale. Consequently, the predominant disposal method for the majority of tannery solid wastes has been, and still is, to landfill (Bauer *et al*, 1977), since this represents a convenient "out of sight, out of mind" policy.

As its name implies, landfill involves disposal of the wastes beneath the ground surface, the tannery wastes often being mixed with municipal refuse before compaction, and covering with a soil layer. Most landfills will accept all forms of tannery solid wastes, including the wastewater treatment sludges (Bauer *et al*, 1977). The latter wastes are not depicted in Figure 1.1 because they are not produced as an entity on their own during the tanning process, but instead refer to those solids removed from the tannery wastewaters during effluent treatment processes (Shuttleworth and Cooper, 1981; Rowswell, 1992).

When solid tannery wastes are disposed of to landfill, the trivalent chromium is generally subject to complexation and precipitation reactions that immobilise the chromium, thereby minimising the likelihood of migration through the landfill. If however, the trivalent chromium becomes oxidised to the hexavalent form, it becomes less susceptible to complexation and precipitation reactions and can migrate through the landfill with the leachate (Martin and Parkin, 1986). This property, together with the solubility of hexavalent chromium, can result in contamination of water aquifers in the vicinity of the landfill. Since groundwater constitutes part of the cycle of water through the environment, the contaminated water can subsequently reach humans, either through drinking water or by moving up the food chain after agricultural use (Lee, 1986). With an increasing world population placing a greater demand on groundwater supply, it is obviously imperative that groundwater contamination be prevented as far as possible (Patrick, 1990).

Although stringent legislation aims to safeguard against Cr^{3+} oxidation, practically, the actual possibility of such oxidation occurring is apparently low. Examination of the redox potentials of

the half-reactions involved in the oxidation of trivalent chromium indicate that the reaction is most favourable under highly basic conditions. A soil pH of twelve is necessary for the formation of significant quantities of Cr^{6+} , provided manganese is present as a catalyst (Shivas, 1980). While the manganese requirement may be readily satisfied (Jones, 1979), soils with a pH greater than nine are rarely encountered. Furthermore, the presence of oxygen is essential for oxidation, and it has been suggested that sunlight may accelerate the reaction. Since all these conditions are unlikely to occur simultaneously in a landfill site, it would seem a safe option for the disposal of tannery solid wastes (Shivas, 1980). Good engineering, site selection and careful operating procedures for landfill can also minimise the potential for leachate generation. However, in spite of all these factors, the possibility of leachate contamination of the groundwater, a situation extremely difficult to reverse and potentially catastrophic, cannot be excluded (Bauer *et al*, 1977; Patrick, 1990).

The presence of chromium is not the only factor influencing land disposal of tannery solid wastes. Both the organic content (Rutland, 1987) and a scarcity of suitable landfill sites (Leather, 1991) are causing growing concern, the latter constraint in particular, making landfill disposal an increasingly expensive option. From an economic point of view, disposal to landfill also represents a great wastage of a potentially reusable resource (Imai and Okamura, 1991). Should chrome-containing wastes ever be reclassified as "hazardous", this will altogether eliminate the option of disposal to landfill in those countries where particularly stringent legislation prohibits the land disposal of hazardous waste (Rutland, 1987). Thus, in general, landfill is becoming less acceptable as a means of disposal and the need to consider other alternatives is obvious.

One possible alternative to landfill disposal would be to channel the solid wastes to a by-product recovery process. Uses proposed for the chrome-tanned shavings and trimmings include: fertiliser, animal feed supplements (Hauck, 1974), reconstituted collagen (for example, for use in the cosmetic industry) (Cot *et al*, 1986), the manufacture of glue (Lipsett, 1982), edible gelatines (Johnston-Banks, 1984), soap, and leatherboard (Hauck, 1974). The splits and leatherdust can be used for reconstituted leathers (Cotance Report, 1991), while the tannery sludges have been used as fertilisers (Wickliff *et al*, 1982).

Although by-product programmes achieve the objective in so far as an option to land disposal of the wastes is concerned, most by-product programmes are targeted towards the use of the organic content of the waste, with the presence of chromium as something of a hindrance. In particular, the concentration of chromium in the solid wastes is too high for direct application in the food and cosmetic industries (Cot *et al*, 1986) and the expensive pretreatment necessary to remove the

chromium limits the marketability of the final product (Johnston-Banks, 1984). In these instances untanned wastes are often the preferred material for use in by-product programmes. The volatile nature of the by-product market further limits its capacity as a dependable alternative to land disposal of the wastes (Bauer *et al*, 1977). The most suitable option open to tanneries therefore appears to be the development of an effective treatment process coupled, if possible, with recovery and/or reutilisation of the chromium. Several possible treatment processes have been developed:

Incineration — This involves a thermal oxidation process where the solid wastes, including the tannery sludges (Beccari *et al*, 1987), are incinerated at high temperatures (900–1200°C) in the presence of excess air (Muralidhara *et al*, 1982). The ash produced contains the chromium in the oxidised hexavalent form and a reduction extraction step is therefore necessary to convert the hexavalent chromium to the trivalent form, for reuse in either the pickle or the tan (Cartier, 1980). Some 60–65% of the chromium in the sludges and solid wastes can be recovered by incineration (Jones, 1977). Although the expense involved in the reduction extraction procedure is a drawback, this can be marginally offset by the utilisation of heat energy produced from the combustion of the organic material, which can be used to supplement existing tannery fuel needs (Muralidhara *et al*, 1982).

Pyrolysis — This represents a variation of the incineration process in that it attempts to overcome the disadvantages of the former by employing lower operating temperatures (300–600°C) and a substoichiometric oxygen environment to prevent oxidation of Cr³⁺ to Cr⁶⁺. The chromium can therefore be recovered from the char produced by means of a simple acid leaching process and the acid solution so produced, directly processed for reuse in the tannery. Some 92% of the chromium can be recovered from the pyrolysis residue. Overall, pyrolysis is the more economically viable of the two thermal degradation processes, although it does have a drawback in that the lower operating temperatures limit its application as far as the tannery sludges are concerned, unless the sludges are first dewatered (Muralidhara *et al*, 1982).

Enzymatic-hydrolysis treatment processes — Various enzymatic-hydrolysis treatment processes have also been reported in the literature, which function with varying degrees of success (Suseela *et al*, 1986; Taylor *et al*, 1990). These processes enable proteolytic degradation of the collagen with concurrent recovery of the chromium. The pH of optimal enzyme activity appears to be the crucial factor as regards ease of chromium recovery. Where the proteolytic enzyme used had optimal activity in the acidic range, the chromium co-solubilised with the hydrolysed protein, making recovery of the chromium more difficult. A subsequent treatment with Ca(OH)₂ was

necessary to separate the chromium from the protein hydrolysate (Suseela *et al*, 1986). Taylor *et al* (1990) developed a enzymatic treatment process that could separate the protein and chromium components of wet blue shavings in a single step. This process employed hydrolysis of the shavings under alkaline conditions, the high pH conditions precipitating the chromium as insoluble chromium hydroxide. Extraction of the chromium cake with dilute acid produced a chromium solution for direct reuse in the pickle step, or alternatively, following precipitation from the acidic solution, a chromium stock which could be used to make up the tan. Similar alkaline hydrolysis investigations were also undertaken by Alves dos Reis and Beleza (1991a and 1991b), the exception being that no proteolytic enzyme was used in these studies. It has previously been reported in literature that lime, by itself, can also cause substantial dissolution of chrome shavings while concurrently separating the chromium from the protein shavings (Chirita, 1976). This is most likely due to base-catalysed cleavage of the protein-protein and protein-chromium bonds. While the merits of such alkaline treatment processes are obvious, utilisation of this process on a large scale (eg. industrial-scale application) would place a high demand on fresh water resources. This process would therefore not be as applicable in an arid country such as South Africa.

RESEARCH OBJECTIVES

The large volumes of highly alkaline effluents discharged from the tannery during the beamhouse operations represent a potential alternative medium for use in alkaline hydrolysis. The high alkalinity of these effluents is due to high concentrations of lime already present. Replacement of fresh water and lime with these alkaline effluents would permit substantial savings in both water resources and chemicals, whilst concurrently utilising a problematic waste product of the tanning industry. This study set out to develop an efficient and cost-effective method for the recovery of chromium from chrome-tanned process solid wastes, generated during the tanning of hides. The primary issues investigated during the study included the following:

- 1) to confirm whether wet blue shavings can be solubilised under simulated alkaline conditions and the chromium recovered in a potentially reusable form.
- 2) to determine the optimum conditions of alkaline hydrolysis for solubilisation of the shavings and chromium recovery, by varying the degree of alkalinity, hydrolysis temperature and duration of hydrolysis, with fresh water and lime as the alkaline medium.
- 3) to investigate the viability of using the highly alkaline beamhouse effluents as substitute media for fresh water and lime in the hydrolysis process.
- 4) to determine whether such an effluent-based treatment process has potential for use on an industrial scale for the treatment of wet blue shavings and, if so, to establish the optimal working conditions for the implementation of such a process.
- 5) to investigate whether this effluent-based process can be applied to other chrome-tanned solid wastes, viz. wet blue splits and finished leather trimmings.
- 6) to assess the chemical nature of the final effluent discharged after alkaline hydrolysis, relative to the initial alkaline effluent used, in order to evaluate the implications of any changes as regards discharge or further treatment requirements.

CHAPTER 2

MATERIALS AND METHODS

1. Solid wastes and effluents.

The solid wastes and effluents utilised in this study were collected from two Eastern Cape tanneries, both of which use a chrome tanning process.

1.1. Solid wastes.

The wet blue splits, wet blue shavings and finished leather trimmings were obtained from Exotan (Pty) Ltd, Port Elizabeth.

1.1.1. Wet blue splits.

The wet blue splits, collected from the splitting and shaving section of the finishing department, were produced from the splitting of the wet blue bovine hide into the upper layer (grain layer) and the lower layer, or flesh side layer, (wet blue split). The splits were cut into workable pieces, 10–15cm² in size, before use in the industrial-scale investigation.

1.1.2. Wet blue shavings.

The wet blue shavings, collected from the splitting and shaving section of the finishing department, were produced from the shaving of wet blue bovine hides and wet blue splits to the correct substance (thickness). The wet blue shavings were stored at 60°C for 24–36 hours before use in the bench-scale alkaline hydrolysis investigations. This removed the moisture from the shavings so that the relevant calculations could be on a dry weight basis. In the industrial-scale investigations, where the increased mass of material precluded desiccation prior to hydrolysis, the moisture content of the shavings was accounted for in the calculations.

1.1.3. Finished leather trimmings.

The finished leather trimmings, collected from the drying section of the finishing department, included trimmings from both sheep and bovine leather. Where necessary, the larger leather trimmings were cut into 10–15cm² pieces before use in the industrial-scale investigation.

1.2. Effluents.

The unhairing effluent and the unhairing wash effluent (hereafter referred to as the wash effluent) were collected from the experimental tannery at Liri Technologies, Grahamstown. The combined processes alkaline effluent (hereafter referred to as the combined effluent) was obtained from Exotan (Pty) Ltd.

1.2.1. Unhairing effluent.

The unhairing effluent, produced during the preparation of the hides for tanning, was collected during discharge of the drum contents following a hair-burn unhairing process. This effluent contained significant quantities of hair, suspended material from the epidermal layer, and lime.

1.2.2. Wash effluent.

Following the unhairing process, hides are repeatedly washed to eliminate excess reagents remaining from this process. The wash effluent, collected from these washings, was of similar composition to the unhairing effluent, but in a far more dilute form.

1.2.3. Combined effluent.

The combined effluent, collected from the primary sulphide oxidation tank for the lime liquors, represented a blend of effluent streams, including:

- liming floats and lime wash effluents (discharged from the Exofell Division)
- unhairing and unhairing wash, liming and lime wash effluents (Exotan Division)
- unhairing and unhairing wash effluents (Exoblue Division).

Being a blend of effluents, the pH was subject to variation, although it was usually in the highly alkaline range (pH 11–12). The effluent was only deemed suitable for use in hydrolysis when the pH was greater than 10.3 (Taylor *et al*, 1990).

2. Effluent clarification.

The effluents were clarified by storage at 4°C prior to use in the bench-scale alkaline hydrolysis investigations. This was particularly important for the unhairing effluent, which contained significant quantities of suspended material, and therefore required a minimum settling period of 6 hours to produce a reasonably clarified effluent. Longer settling periods (> 6 hours) were even more beneficial. A 30 minute settling period was more than sufficient for the wash and the combined effluents. In each instance, the clarified effluents were decanted for use in hydrolysis, the sediments were discarded.

3. Moisture content.

Quantities of wet blue shavings were weighed accurately, dried at 60°C for 24–36 hours and reweighed. The moisture content was determined by difference and expressed as a percentage. Periodic analysis of the moisture content of the crude wet blue shavings indicated a slight variation from batch to batch and within each batch of shavings produced. The mean moisture content was found to be $52 \pm 2.6\%$ (w/w).

4. pH measurement.

The pH measurements were made on a digital pH meter quoting two decimal places.

5. Bench-scale alkaline hydrolysis.

The alkaline hydrolysis process was first investigated on a bench-scale level where the conditions of hydrolysis were optimised. The optimum conditions were established for both solubilisation of the shavings during hydrolysis and for recovery of chromium from the solid residues after hydrolysis. All hydrolysis procedures and ensuing analytical determinations (excluding industrial scale solubilisation, size reduction and chromium recovery investigations) were conducted in triplicate.

5.1. Optimisation of the conditions of alkaline hydrolysis.

In each instance the general hydrolysis procedure is outlined first, the details provided thereafter.

5.1.1. Alkaline hydrolysis using fresh water and lime.

Desiccated wet blue shavings (4.0g) were added to flasks containing 300mL of fresh water heated to 50–80°C. Quantities of lime (as calcium hydroxide ($\text{Ca}(\text{OH})_2$)) were added to the flasks to produce concentrations of 0–12% (w/w of lime/shavings). The contents of each flask were mixed and the pH recorded. The samples were shaken in an orbital shaker at approximately 100rpm for 1–24 hours at the originally determined temperature. Temperature variation was $\leq 2^\circ\text{C}$ in all bench-scale investigations. Upon termination of alkaline hydrolysis, the pH of the media were recorded and the samples filtered using Whatman # 541 filter papers. Whatman # 541 filter papers were used in all subsequent hydrolysis investigations as well. The filter papers and solid residues were dried at 60°C and weighed. Portions of the dried solid residues (0.5g) were retained for acid wash treatment (refer to section 7 below). The alkaline hydrolysis filtrates and solid residues were analysed for chromium content (section 8 below). The solubilisation of the shavings during hydrolysis was assumed to be the difference between the initial dry weight of the crude shavings (i.e. 4.0g) and the dry weight of the solid residues obtained. However, part of the lime added remained insoluble throughout the hydrolysis procedure and contributed to the weight of the solid residues. The percentage calcium content of the hydrolysis solid residues was therefore determined (section 6 below) and the residue weights adjusted accordingly. The corrected weights of the solid residues were used to determine the percentage solubilisation of the shavings. Figure 2.1 summarises, by flow diagram, the general procedure outlined above. A similar general procedure was followed in all subsequent hydrolysis investigations described.

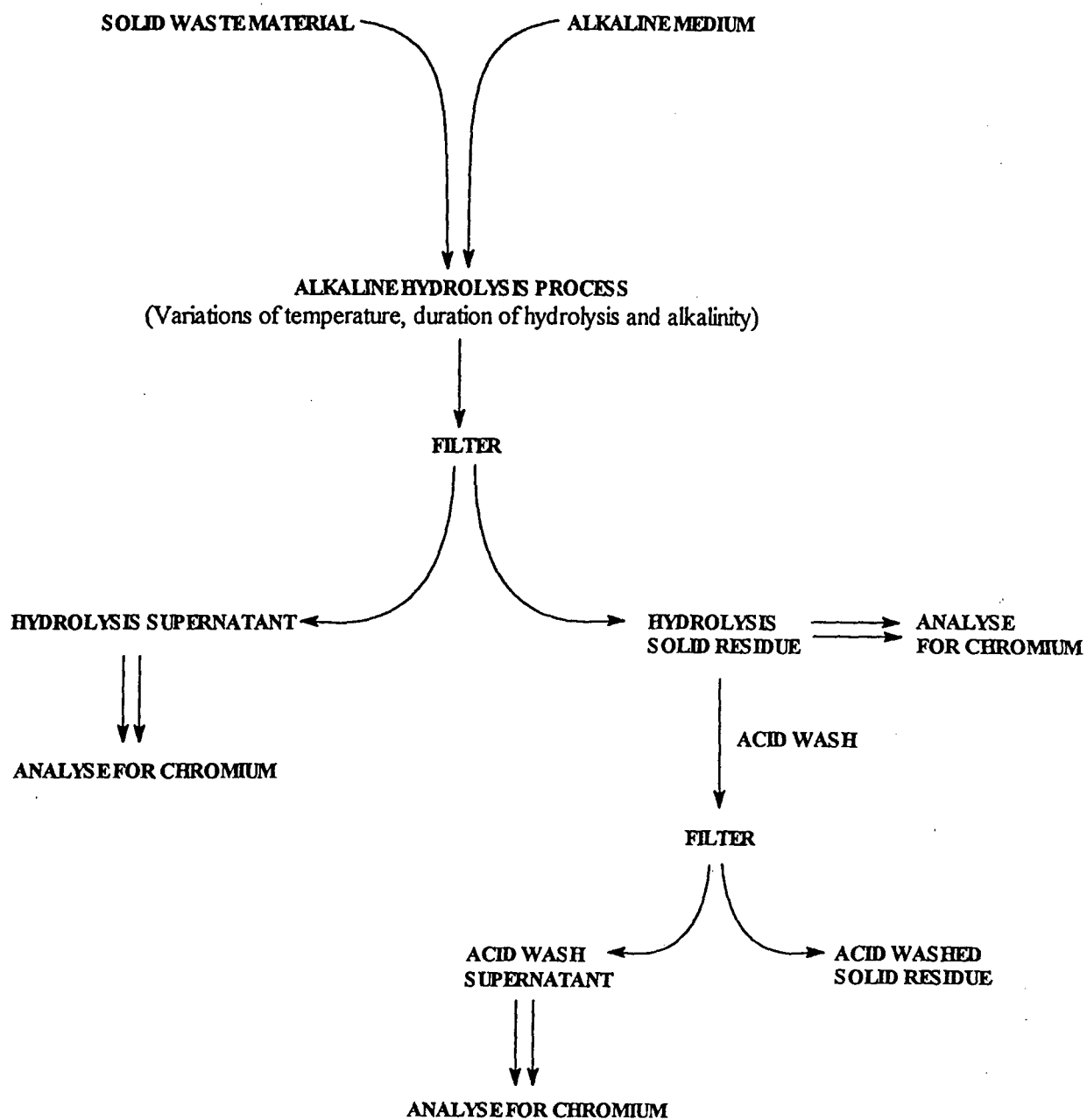


Figure 2.1. The general procedure followed for the dechroming of tannery solid waste material.

5.1.1.1. Optimisation of the degree of alkalinity (% lime).

Lime was added to the shavings to produce concentrations of 0, 4, 6, 8, 10 and 12%, and the flasks incubated at 65°C for 12 hours.

5.1.1.2. Optimisation of the hydrolysis temperature.

The optimal percentage lime (established in 4.1.1.1.) was added to all flasks, and the flasks incubated at 50, 60, 70 and 80°C for 12 hours.

5.1.1.3. Optimisation of the hydrolysis period.

The optimal percentage lime (established in 4.1.1.1.) was added to all flasks, and the flasks incubated at the optimal hydrolysis temperature (established in 4.1.1.2.) for 1, 2, 6, 12 and 24 hours.

5.1.2. Alkaline hydrolysis using the individual process effluents (unhairing effluent and wash effluent).

Desiccated wet blue shavings (4.0g) were added to flasks containing 300mL of clarified effluent pre-heated to 50–80°C. The contents were mixed and the pH of the media recorded. The flasks were shaken in an orbital shaker at approximately 100rpm for 1–24 hours at the originally determined temperature. Upon termination of alkaline hydrolysis the pH of the media were recorded and the samples filtered. The filter papers and solid residues were dried at 60°C and weighed. Portions of the dried solid residues (0.5g) were retained for acid wash treatment and the alkaline hydrolysis filtrates and solid residues analysed for chromium content. Control samples containing 300mL of clarified effluent alone were incubated in an identical manner to the above, to correct for the excess weight contributed to the solid residues by the suspended and/or dissolved materials in the effluents. The percentage solubilisation of the shavings during hydrolysis was calculated as before (section 4.1.1 above).

5.1.2.1. Optimisation of the hydrolysis temperature.

The flasks were incubated at 50, 60, 70 and 80°C for 12 hours.

5.1.2.2. Optimisation of the hydrolysis period.

The flasks were incubated at the optimal hydrolysis temperature (established in 4.1.2.1.) for 1, 2, 6, 12 and 24 hours.

5.2. Scaled-up investigations of alkaline hydrolysis.

Three ten-fold scaled-up investigations were undertaken, two of which utilised the optimum hydrolysis conditions established above. The first investigation used fresh water and lime, the second, the more effective of the individual process effluents. The third scaled-up investigation utilised the combined effluent, adopting the optimum hydrolysis conditions established for the more effective individual process effluent.

Desiccated wet blue shavings (40.0g) were added to flasks containing 3 000mL of either fresh water, or clarified effluent, pre-heated to the optimum temperature. The determined optimum percentage lime was added where fresh water was used. The pH readings of the hydrolysis media were recorded and the flasks incubated in an orbital shaker at approximately 100rpm for the established duration of hydrolysis. Upon termination of hydrolysis, the final pH readings were recorded and the samples filtered. The filter papers and solid residues were dried at 60°C and weighed. A portion from each respective dried solid residue (0.5g) was retained for acid wash treatment. The alkaline hydrolysis filtrates and dried solid residues were analysed for chromium content. The percentage solubilisation of the shavings was calculated as previously described for the fresh water and effluent analyses (sections 4.1.1. and 4.1.2. above). In each instance the excess weight contributed to the solid residue by the lime (fresh water analysis), or the suspended and/or dissolved materials (effluent analysis), was corrected for.

6. Industrial-scale alkaline hydrolysis.

The hydrolysis procedures were undertaken at Exotan (Pty) Ltd, Port Elizabeth. The combined effluent was the sole alkaline effluent utilised as a hydrolysis medium.

6.1. Reaction vessel.

A fat pot of dimensions: 2.45m (length), 1.20m (width) and 1.10m (depth), (total liquid capacity 3 234L) was used. Heat and agitation were provided by steam which entered the reaction vessel *via* a pitted pipe, which ran the approximate length of the tank along its base. A valve allowed for control of the amount of steam entering the tank. An outlet tap at the base of the tank enabled discharge of the tank contents upon termination of alkaline hydrolysis. Plate 2.1 illustrates a posterior view of two adjoining identical fat pots, the reaction vessel on the right-hand side representing the specific vessel used in these investigations.

6.2. Solid waste material - wet blue shavings.

Quantities of 50, 100, 150 and 220kg (wet weight) of wet blue shavings were added to the reaction vessel. Fresh effluent from the primary sulphide oxidation tank (Plate 2.2) was added

to the bin (Plate 2.3), to a final volume of approximately three quarters of the total bin capacity. Steam was introduced to the reaction vessel in sufficient quantity to maintain the contents at the approximate boiling point of the effluent. Plate 2.4 illustrates the hydrolysis reaction in progress. 1L and 5L grab samples were collected for analysis. The first sample was drawn immediately the effluent reached 70°C. Additional samples were drawn thereafter at 15 minute intervals for the first hour of heating (50kg analysis excluded) and then hourly for a total heating period of 6 hours. The pH (universal pH indicator) and temperature of the effluent were recorded at each sampling time, the latter a routine assessment to maintain the required temperature. At the end of the 6 hour heating period steam heating was discontinued and the contents settled prior to discharge from the bin. The clarified effluent was discharged to an on-site wastewater treatment plant and the settled solid residue to a solid waste collection sump for removal.

6.2.1. Analysis of the 1 litre sample volumes.

The 1L sample volumes were filtered and the solid residues dried at 60°C and weighed for solubilisation determinations. A 0.5g portion of each dried solid residue was retained for acid wash treatment. The alkaline hydrolysis filtrates and solid residues were analysed for chromium content. Determination of the percentage solubilisation of the shavings during alkaline hydrolysis assumed homogeneous mixture of the shavings at all times. The dry weight of the sample solid residues was related to the hypothetical dry weight of an equivalent 1L sample volume of shavings and effluent at zero hour reaction time. Solubilisation of the shavings was assumed to be the difference between the two dry weights. The displacement of the effluent by the shavings at the onset of alkaline hydrolysis was ignored in all instances, as was the excess weight contributed to the solid residues by the suspended and/or dissolved material in the effluent. The latter was considered insignificant on an industrial scale.

6.2.2. Analysis of the 5 litre sample volumes.

The 5L sample volumes were filtered through a stainless steel sieve (pore size 4mm²). The material retained in the sieve for each sample time was collected, dried at 60°C, and weighed. The determination of size reduction of the shavings with time during alkaline hydrolysis also assumed a homogeneous mixture of the shavings at all times. The dry weight of the solid residues was related to the hypothetical dry weight of an equivalent 5L sample volume of shavings and effluent at zero hour reaction time. The difference between the two dry weights was assumed to represent material small enough to pass through the sieve apertures (i.e. the protein solubilised during alkaline hydrolysis was ignored). Size reduction of the shavings with time was expressed as a percentage of solid material less than 4mm² in size for each time period.



Plate 2.1. Reaction vessel utilised for hydrolysis of the solid wastes in the industrial-scale investigations.



Plate 2.2. The sulphide oxidation tank (circular tank) from which the effluent was removed for use in hydrolysis. Also visible are the two settling cones in which the alkaline effluents were initially settled following discharge from the tannery.



Plate 2.3. Introduction of the effluent to the reaction vessel prior to hydrolysis.



Plate 2.4. The hydrolysis reaction in progress.

6.3. Solid waste material - wet blue splits and finished leather trimmings.

Quantities of wet blue splits and finished leather trimmings were cut into 10–15cm² pieces to provide a smaller substrate for hydrolysis. The cut material was transferred to the reaction vessel and fresh effluent from the primary sulphide oxidation tank added, to a final volume of approximately three quarters of the total bin capacity. Steam was introduced to the reaction vessel in sufficient quantity to maintain the effluent and contents at the approximate boiling point. A 1L sample volume of effluent, a sample of wet blue splits, and one of finished leather trimmings were collected immediately the effluent reached 70°C. Additional samples were collected at 15 minute intervals for the first hour of heating and then hourly for a total initial heating period of 6 hours. The pH and temperature of the effluent were recorded at each sampling time. Steam heating was discontinued overnight (a 15 hour period) but the contents of the bin were not discharged. After overnight settling, the effluent was reheated to its approximate boiling point for a further 3 hours (i.e. a total hydrolysis period of 24 hours). A final 1L sample of effluent, a sample of wet blue splits, and one of finished leather trimmings were collected. The final pH and temperature of the effluent were recorded. The steam heating was discontinued and the contents of the bin settled prior to discharge. The clarified effluent was discharged to an on-site wastewater treatment plant and the settled solid residue to a solid waste collection sump for removal.

6.3.1. Analysis of the samples.

The 1L sample volumes of effluent were filtered and the filtrates analysed for chromium content. Individual portions (6cm x 2cm), where possible, of wet blue splits and finished leather trimmings for each sampling time were dried at 60°C for 24–36 hours. A 0.5g quantity of each dried solid residue was retained for acid wash treatment. The dried wet blue splits and leather trimmings were analysed for chromium content, the outer, middle and innermost portions of each sample analysed individually and the respective values averaged.

7. Calcium content of the alkaline hydrolysis solid residues from the lime optimisation study.

The calcium content of the solid residues was determined following digestion of the residues in concentrated HNO₃. Approximately 0.5g of each dried solid residue was weighed accurately and placed in a kjeldahl flask. Equivalent 20mL volumes of deionised water and concentrated HNO₃ were added and the sample mixtures heated to boiling in a fume cupboard. After heating had reduced the volume in the flasks to approximately 20mL, the mixtures were cooled, and washed into standard volumetric flasks with deionised water and the calcium content determined by atomic absorption spectrophotometry. A Varian AA–1275 series atomic absorption spectrophotometer was used in this and all subsequent analytical quantifications requiring atomic absorption

spectrophotometry. The precision of measurement of the spectrophotometer was within 0.01mg.L^{-1} .

Calculation:

$$\% \text{ calcium} = \frac{r \times v \times 100}{10^6 \times w}$$

where:

r = reading on the atomic absorption spectrophotometer (mg.L^{-1})

v = volume of the diluted sample (mL)

w = weight (g)

8. Acid wash procedure.

A 50mL volume of 1M H_2SO_4 was added to 0.5g of desiccated sample and stirred periodically over 4 hours. The acidic supernatant was filtered using Whatman GF/A filter paper and retained. A fresh 50mL portion of acid was added to the solid residue and stirred periodically for a further 4 hours. Both supernatant and residue were filtered through the original GF/A filter paper used and the two acidic filtrates combined. The filtrates were analysed for chromium content.

8.1. Quantification of the chromium recovered.

Calculation of the chromium recovered was always based on mass balance of the chromium before and after acid wash treatment, as the initial chromium present in the shavings was only determined periodically. Firstly, the total chromium present in the flask immediately after alkaline hydrolysis was obtained by adding the quantity of chromium determined to be present in the solid residue, to the chromium lost in the hydrolysis filtrate. The chromium initially present in a 0.5g representative sample of solid residue prior to acid wash treatment (A) was then determined. The mass of chromium recovered from this 0.5g sample by acid wash treatment (B) was expressed as a percentage of the chromium present in the initial shavings (A).

9. Determination of chromium.

Chromium was determined according to the official wet oxidation method (method SLC.8) of the Society of Leather Trades' Chemists (1965) for the determination of chromium in leather [Appendix I(a)]. The chromium concentration was calculated as either mg.L^{-1} total chromium (alkaline hydrolysis filtrates and raw effluents), or as percentage total chromium (crude solid waste materials (i.e. before alkaline hydrolysis), alkaline hydrolysis solid residues and acid wash treatment supernatants).

10. Chemical analysis of the effluents.

The following chemical analyses were conducted in triplicate for each effluent, the results tabulated in the text representing the average of the three values. Detailed methodologies of the individual chemical tests performed are included in Appendix II.

10.1. Storage of the effluents.

The effluents were stored at 4°C during analysis. All analyses were performed using effluents which had been stored for less than 14 days.

10.2. Conductivity.

The conductivity of the effluent was measured with a dds 200 conductivity meter. The conductivity was expressed as milliSiemens per metre ($\text{mS}\cdot\text{m}^{-1}$).

10.3. Alkalinity.

Alkalinity was determined according to the official method of the Department of Water Affairs, South Africa (1975). The end point pH values adopted for the analysis were as suggested in *Standard Methods for the Examination of Water and Waste-Water* (1981). The combined method is outlined in Appendix I(b). Alkalinity was expressed as $\text{mg}\cdot\text{L}^{-1}$ calcium carbonate (CaCO_3) relative to the end point pH.

10.4. Permanganate Value (PV).

The PV was determined according to the official method as published in the South African Government Gazette (1969), except:

— 0.0125N sodium thiosulphate was used as the titrant, [Appendix I(d)].

The PV was expressed as $\text{mg}\cdot\text{L}^{-1}$ PV.

10.5. Chemical Oxygen Demand (COD).

The COD was determined according to the method employed by Liri Technologies [Appendix I(c)]. This method is an adaptation of the standard dichromate reflux method (*Standard Methods for the Examination of Water and Waste-Water*, 1981). The COD was expressed as $\text{mg}\cdot\text{L}^{-1}$ COD.

10.6. Nitrogen (as ammonia).

Ammonia nitrogen was determined according to the official method as published in the South African Government Gazette (1969) for the determination of free and saline ammonia, except:

— the aliquot was neutralised by the addition of caustic soda

— magnesium oxide was not added

- the strength of the H₂SO₄ titrant was on the basis of the amount of ammonia perceived to be present, [Appendix I(h)].

The ammonia concentration was expressed as mg.L⁻¹ ammonia nitrogen.

10.7. Nitrogen (as nitrate).

Nitrogen in the form of nitrate was determined according to the official method as published in the South African Government Gazette (1969), except:

- the distillate from the determination of ammonia nitrogen was not tested with Nessler solution
- the strength of the H₂SO₄ titrant was on the basis of the amount of nitrate perceived to be present, [Appendix I(i)].

The nitrate concentration was expressed as mg.L⁻¹ nitrate nitrogen.

10.8. Nitrogen (as Total Kjeldahl Nitrogen) (TKN).

The total amino nitrogen (as TKN) was determined according to the standard kjeldahl method (method SLC.7) of the Society of Leather Trades' Chemists (1965), except:

- the sample was not heated in concentrated H₂SO₄ prior to addition of the catalyst mixture. Instead the H₂SO₄ was incorporated into a liquid catalyst mixture (hereafter referred to as the digestion mixture)
- carborundum powder was added instead of 1% phenolphthalein solution, [Appendix I(j)].

The total amino nitrogen content was expressed as mg.L⁻¹ nitrogen.

10.9. Sodium.

A suitable aliquot of the effluent was diluted with deionised water and the sodium content determined by atomic absorption spectrophotometry. The sodium concentration was expressed as mg.L⁻¹ sodium.

10.10. Calcium.

A suitable aliquot of the effluent was diluted with deionised water and the calcium content determined by atomic absorption spectrophotometry. The calcium concentration was expressed as mg.L⁻¹ calcium.

10.11. Sulphate.

Sulphate was determined according to the standard gravimetric method with ignition of residue (*Standard Methods for the Examination of Water and Waste-Water*, 1981), except:

- silica removal prior to the precipitation of barium sulphate was not necessary

- the barium sulphate precipitate was not mixed with ashless filter paper pulp
- chloride was not assayed
- the filter and precipitate were ignited at 600°C for 4 hours, [Appendix I(g)].

The sulphate concentration was expressed as mg.L⁻¹ sulphate.

10.12. Sulphide.

Sulphide was determined according to the standard method (method SLM.4\2) of the Society of Leather Trades' Chemists (1965) [Appendix I(f)]. This method is intended for the determination of sulphide in alkaline liquors and unhairing paints. The sulphide concentration was expressed as mg.L⁻¹ sodium sulphide (Na₂S).

10.13. Chloride.

Chloride was determined according to the method employed by Liri Technologies for the determination of chloride in lime and dehairing liquors [Appendix I(e)]. This method is an adaptation of the standard argentometric method for the analysis of chloride (*Standard Methods for the Examination of Water and Waste-Water*, 1981). The chloride concentration was expressed as mg.L⁻¹ chloride.

10.14. Soap, oil or grease.

The soap, oil or grease content was determined according to the method employed by Liri Technologies [Appendix I(k)]. This method is an adaptation of the official method as published in the South African Government Gazette (1969). The soap, oil or grease content was expressed as mg.L⁻¹ soap, oil or grease.

10.15. Settling rate.

A 1 000mL volume of effluent was placed in a graduated 1 000mL Imhoff settling cone and the contents settled under gravity for 2 hours. The settling rate was expressed as mL of settled effluent in two hours. In one particular instance the settling period was extended to 48 hours, the settling profile represented graphically in this case.

11. Statistical analyses.

The standard error of the samples was calculated according to Porkess (1988) and represents the reasonable difference between a sample mean and the true mean. The equation followed is outlined below.

Calculation:

$$\text{Standard error} = \frac{\sigma}{\sqrt{n}}$$

where: σ = standard deviation

\sqrt{n} = square root of the sample size (n)

CHAPTER 3

OPTIMISATION OF LIME-BASED ALKALINE HYDROLYSIS

1. Introduction.

The investigation into the use of the beamhouse effluents as alternative hydrolysis media for the detanning of chrome-tanned solid wastes started with a preliminary investigation to confirm the earlier literature reports of Taylor *et al* (1990) and Alves dos Reis and Beleza (1991a) that chrome-tanned solid wastes could be hydrolysed under alkaline conditions and the chromium recovered by an acid wash procedure. In the preliminary investigation, alkaline conditions were provided by the addition of $\text{Ca}(\text{OH})_2$, selected on the basis of its low cost and low toxicity (Bataille *et al*, 1983), but also because it represents the principal alkaline constituent of the beamhouse effluents (Bailey *et al*, 1981).

Wet blue shavings, as the solid waste substrate, were subjected to alkaline hydrolysis, with the degree of alkalinity, hydrolysis temperature and hydrolysis period varied, in order to establish the optimum conditions of hydrolysis. Optimum conditions were selected to favour solubilisation of the shavings and the degree of chromium recovery. A scaled-up investigation, using the established optimum hydrolysis conditions, was also conducted.

2. Results.

2.1. Analysis of crude wet blue shavings.

In order to establish a benchmark against which the effect, if any, of alkaline hydrolysis on the shavings could be compared, the chromium content of the crude shavings and the percentage chromium recoverable by acid wash treatment (without the benefit of preceding alkaline hydrolysis) was determined. The chromium content of the crude shavings is hereafter referred to as the initial chromium content of the shavings.

2.1.1. Initial chromium content of wet blue shavings.

Periodic analysis of the initial chromium content of the shavings indicated slight variation from batch to batch and within each batch of shavings produced. The initial chromium content of the shavings utilised in each hydrolysis investigation was therefore determined by mass balance calculation. The mean value so obtained for each investigation ranged between 1.5 and 3.0% and can be seen tabulated in Appendix II, Table I.

2.1.2. Chromium recovery by acid wash.

Only 24% of the chromium present in the crude wet blue shavings was recovered by acid wash treatment prior to alkaline hydrolysis. It is most probable that this primarily represents solubilisation of the excess chrome tannage still weakly associated with the protein substrate of the shavings. The development of a blue colour to the initially colourless acid wash medium, observed in the present and subsequent acid wash investigations, was found to be synonymous with the presence of solubilised chromium.

2.2. Optimum conditions for alkaline hydrolysis.

2.2.1. Degree of alkalinity.

Test concentrations of lime ranging from 0–12% were investigated. The almost neutral initial pH (pre-hydrolysis pH) of the 0% lime sample (pH 6.89, Appendix II Table II) enabled this sample to serve as a control sample to indicate the effect of non-alkaline hydrolysis conditions on both solubilisation and chromium recovery.

2.2.1.1. Solubilisation of the shavings during alkaline hydrolysis.

The effect of lime concentration on solubilisation of the shavings is shown in Figure 3.1. When added, part of the lime remained insoluble throughout the hydrolysis process and contributed to the weight of the solid residue (hydrolysed shavings) obtained. Since quantification of the extent of solubilisation was carried out on a solid residue dry weight basis, it was necessary to correct for the excess weight contributed by the lime. This was accounted for as outlined in Table 3.1. The endogenous calcium contained within the shavings (0.10% calcium, 0% lime, Table 3.1) was deducted to give the 4–12% sample values represented.

Table 3.1. Calcium concentrations of the alkaline hydrolysis solid residues from the lime optimisation study.

concentration of lime added (%)	calcium concentration of the residue (%)
0	0.10 ± 0.01
4	1.18 ± 0.06
6	1.75 ± 0.07
8	2.51 ± 0.14
10	6.19 ± 0.01
12	8.37 ± 0.11

Table 3.1 was used in a similar manner to quantify the solubilisation of the shavings attained in subsequent investigations described in this chapter, where $\text{Ca}(\text{OH})_2$ was again added as the alkaline ingredient during hydrolysis.

Although the first 4% quantity of lime added to the shavings raised the initial pH to well within the alkaline range (pH 10.44), it was only when concentrations of lime in excess of 6% were attained that the lime appeared to enhance solubilisation. This corresponded to an initial pH of above 11.17 (6% lime). The addition of more than 10% lime resulted in minimal further improvement in the percent solid shavings dissolved, the 70.9% solubilisation of the 10% lime sample an effective 3.5 times that of the control (0% lime produced 20.5% solubilisation). The effect of heat and agitation on solubilisation is illustrated by the non-alkaline reaction conditions of this control.

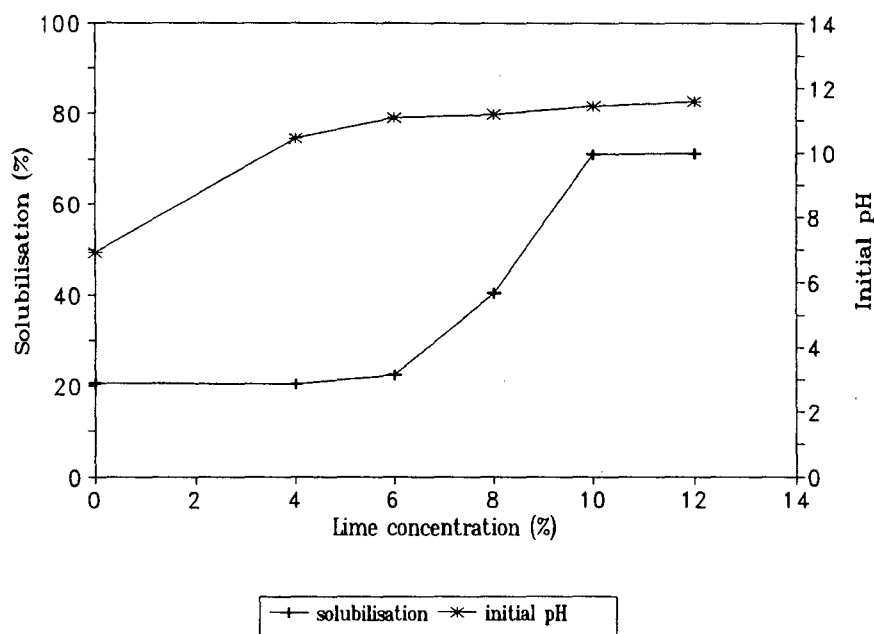


Figure 3.1. Effect of lime concentration and the resultant initial pH on the solubilisation of wet blue shavings.

The general manner in which solubilisation of the shavings progressed remained essentially uniform in all investigations undertaken. This is described with the aid of Plate 3.1 which illustrates the wet solid residues of the shavings hydrolysed in the 0–12% lime solutions. Prior to alkaline hydrolysis, the fibrous wet blue shavings were light blue in colour. During the early stages of solubilisation this colour darkened to a green colour, which became progressively darker

as the protein component of the shavings solubilised and the chromium concentrated. Physical degradation of the shavings was initially only apparent on the peripheries of the shavings, observed as increasingly irregular edges (0–6% lime). With further degradation, the shavings became significantly narrowed and spiralled (8% lime). Reduction in the length of the shavings also occurred, due to dissociation of fragments from the shavings, the latter degrading further as solubilisation progressed. The fibrous nature of the crude shavings decreased proportionately with time throughout hydrolysis and the shavings became more gelatinous. Maximal protein solubilisation was characterised by a total breakdown in the physical structure of the shavings, with the residue consisting only of a fine dark-green silt-like material (10 and 12% lime).

2.2.1.2. Chromium content of the alkaline hydrolysis fractions.

The chromium concentrations of the 0–12% lime hydrolysis filtrates and solid residues are compared in Figure 3.2 to show the apportionment of chromium during hydrolysis. The very low chromium concentrations of the hydrolysis filtrates ($0.30\text{--}0.52\text{mg.L}^{-1}$) indicate that virtually all of the chromium contained within the crude shavings remained associated with the solid residues. This was true even for the control sample (0.30mg.L^{-1} filtrate chromium) where the post-hydrolysis pH of the medium (final pH) was considerably lower than those recorded for the lime-containing samples (0% lime, final pH 4.46 vs 4–12% lime, final pH 7.69–10.44). The increase in the percentage chromium content of the solid residues is due to solubilisation of the protein component of the shavings. The chromium was concentrated in the solid residues between 1.1 and 3.3 fold (2.3% initial chromium content of the shavings, Appendix II Table I).

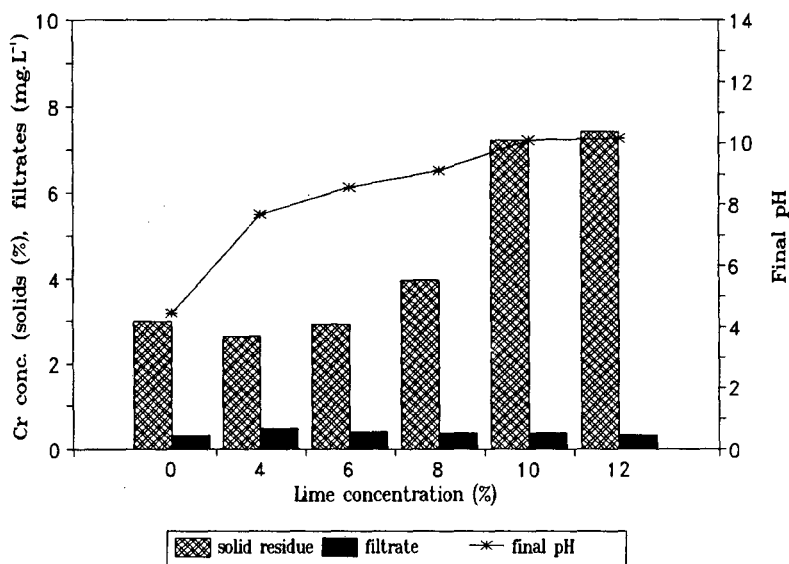


Figure 3.2. Effect of lime concentration on the chromium concentrations of the hydrolysis filtrates and solid residues.

2.2.1.3. Chromium recovery by acid wash.

The effect of the lime concentration on the recovery of chromium from the solid residues is shown in Figure 3.3, together with the solubilisation of the shavings attained during alkaline hydrolysis. Virtually double the recovery of chromium occurred from the shavings hydrolysed under alkaline conditions (4–12% lime) compared to the control (non-alkaline conditions) (85–88% recovery vs 45% recovery). It is also evident from Figure 3.3 that similar chromium recoveries were obtained for the 4–12% lime samples, despite considerable differences in the percentage solubilisation of the shavings attained during alkaline hydrolysis. Over 84% of the chromium was recovered from the 4% lime sample (20.3% solubilisation) compared to 87% recovery from the 12% lime sample (71.1% solubilisation).

The bleached appearance of the solid residues after acid washing (Plate 3.2) further illustrates the removal of chromium from the residues. This detanned appearance was more pronounced where the shavings had not undergone much solubilisation during alkaline hydrolysis, namely for the 4% and 6% lime samples. The 8–12% lime samples remained as brown residues dispersed over the filter papers, with very little actual solid material remaining. This is due to the more advanced protein solubilisation of the 8–12% lime samples (Figure 3.3), resulting in solid residues after alkaline hydrolysis consisting primarily of precipitated chromium. This was then solubilised during acid washing.

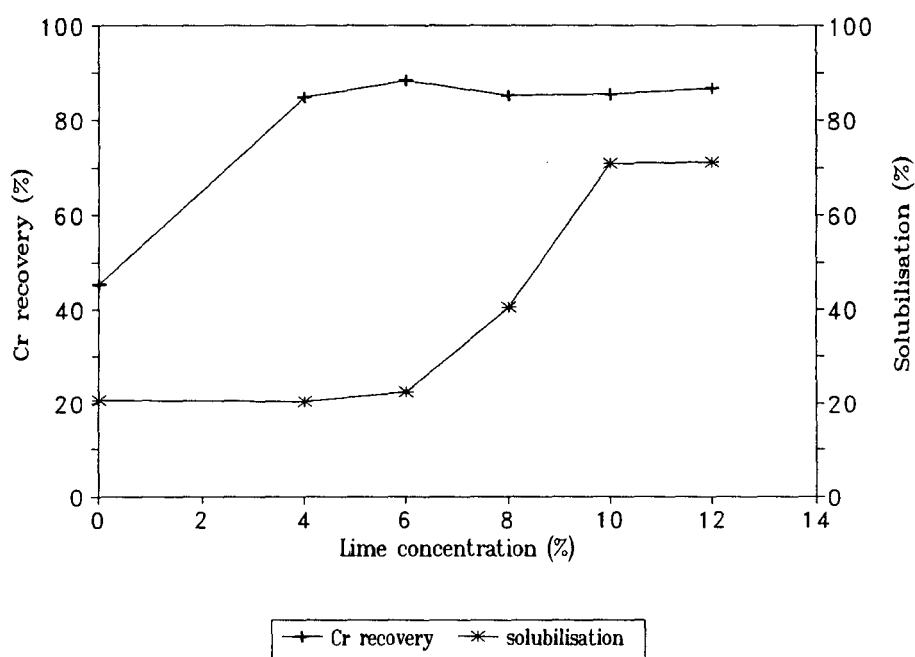


Figure 3.3. Comparison of the effect of lime concentration on the solubilisation of wet blue shavings (alkaline hydrolysis) and on the recovery of chromium (acid wash).

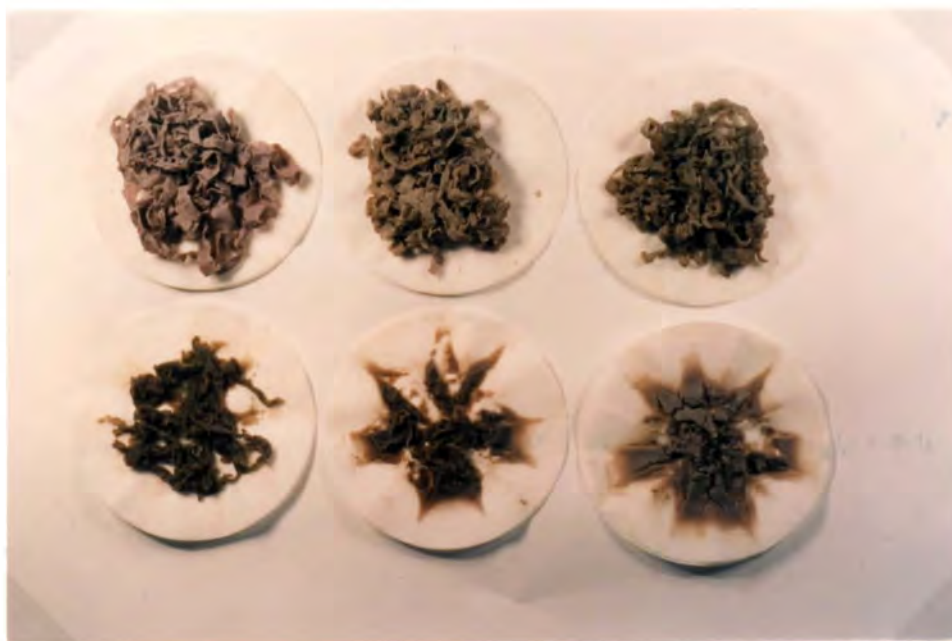


Plate 3.1. Desiccated solid residues of the wet blue shavings hydrolysed in 0–12% lime solutions.



Plate 3.2. Acid wash supernatants and solid residues of the lime optimisation study.

The noticeable increase in the colour intensity of the blue acid wash supernatants (pale blue, 0% lime—dark blue-green, 10 and 12% lime) was due to increasing concentrations of chromium recovered into the supernatants. The darker blue colour was particularly evident in the 8–12% lime samples where the higher degree of solubilisation (Figure 3.3), and ultimately, the higher chromium concentration of the solid residues (Figure 3.2), made available more chromium per unit weight of solid residue for solubilisation during acid wash.

2.2.2. Hydrolysis temperature.

The optimum temperature for the hydrolysis reaction was established by increasing the temperature of incubation from 50–80°C in ten degree increments of temperature. The optimum concentration of lime established in the previous study (10%) was added to all sample flasks.

2.2.2.1. Solubilisation of the shavings during alkaline hydrolysis.

Figure 3.4 shows the effect of hydrolysis temperature on the solubilisation of wet blue shavings, and on the chromium concentrations of the resultant hydrolysis filtrates. The initial pH of the hydrolysis samples ranged from 10.38–11.13 (Appendix II, Table II). The most marked effect of the hydrolysis temperature on solubilisation occurred between 50 and 70°C. Less than 14% solubilisation (13.9% solubilisation) occurred for hydrolysis at 50°C, but with an increase in the hydrolysis temperature to 70°C, 71.9% of the shavings were solubilised. This represented a 5.2 fold increase in the percentage solubilisation attained. Hydrolysis at 80°C resulted in minimal further improvement in the percent solid shavings solubilised (73.0% solubilisation). Variation of the hydrolysis temperature between 50 and 80°C did not cause any substantial increase in the concentration of chromium lost in the hydrolysis filtrates. This is shown by the low chromium concentrations of the filtrates (0.19–0.50mg.L⁻¹) (filtrate final pH range 9.62–10.75, Appendix II Table II).

Plate 3.3 shows the extent of physical degradation of the shavings during alkaline hydrolysis over the temperature range studied. The 50°C residue (13.9% solubilisation) still closely resembled the parent shavings in both colour (light blue-grey) and physical structure (ribbon-shaped). Increase in the hydrolysis temperature to 60°C resulted in degradation of the shavings to a dark green, friable residue (when dry), which consisted of shavings considerably reduced in length and with a very small proportion of fibrous material still evident. Further increase in the hydrolysis temperature (70 and 80°C) resulted in more advanced degradation of the shavings into fragments of the crude material. The 70 and 80°C solid residues were even more friable and contained no residual fibrous material.

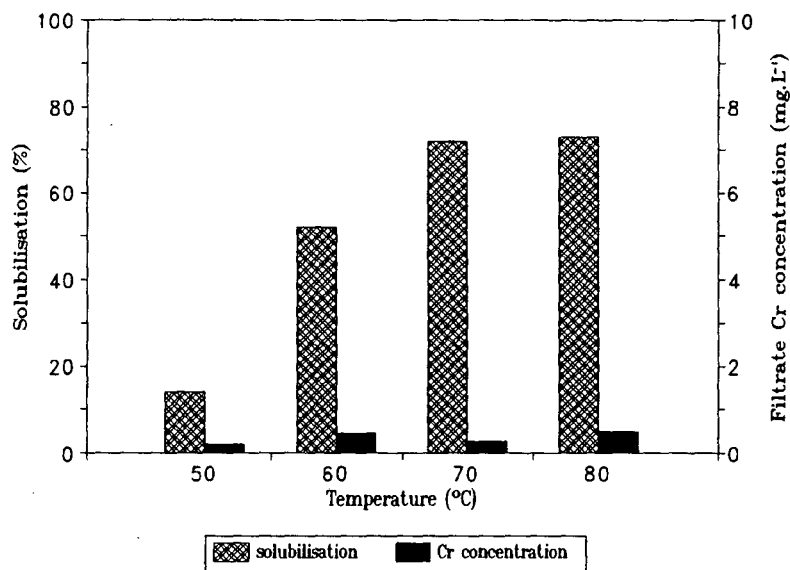


Figure 3.4. Comparison of the effect of hydrolysis temperature on the solubilisation of wet blue shavings and on hydrolysis filtrate chromium concentrations.

2.2.2.2. Chromium content of the alkaline hydrolysis fractions.

The low chromium concentrations of the hydrolysis filtrates, shown in Figure 3.4 to be between 0.19 and 0.50mg.L⁻¹, indicate that the chromium remained associated with the solid residues for all hydrolysis temperatures investigated. Figure 3.5 shows the chromium concentrations of the solid residues and illustrates the concentration of the chromium in these residues as solubilisation progressed. The chromium concentrations of the solid residues ranged from 2.6 to 8.8%, the chromium concentrated 1.2–4.0 fold relative to the initial chromium content of the shavings (2.2% chromium, Appendix II, Table II).

2.2.2.3. Chromium recovery by acid wash.

Figure 3.6 shows the effect of hydrolysis temperature on the recovery of chromium from the solid residues. Neither the temperature at which the shavings were incubated, nor the associated degree of protein solubilisation that occurred (alkaline hydrolysis) had any significant effect on the percentage chromium recovered. Between 92 and 100% of the chromium was recovered from all samples, 92% from the 50°C sample (13.9% solubilisation, Figure 3.4) compared to 100% from the 70 and 80°C samples (>71% solubilisation in each case, Figure 3.4). This represents an increase of only 8% in the chromium recovered, for an over 500% increase in the solubilisation obtained during alkaline hydrolysis. Plate 3.4 illustrates the acid wash supernatants and solid residues of the hydrolysis temperature optimisation study.

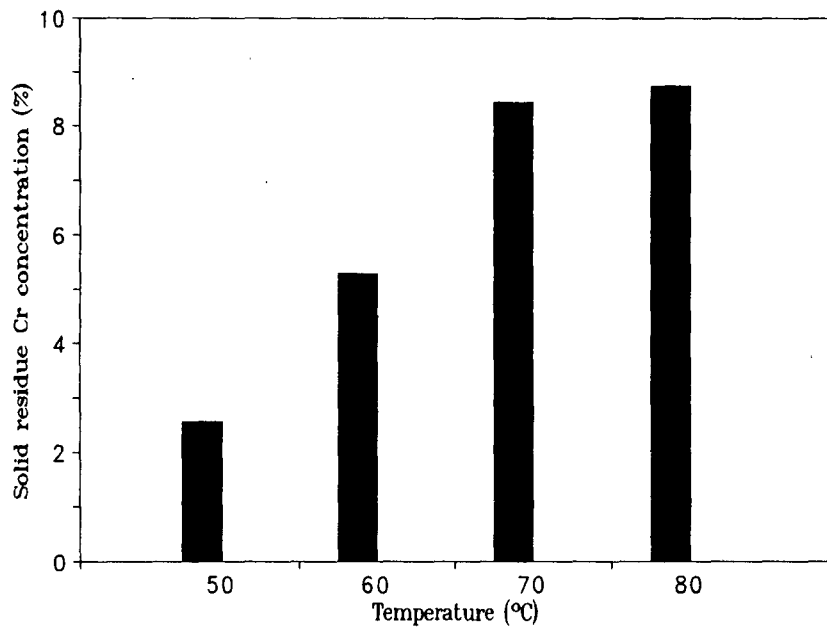


Figure 3.5. Effect of hydrolysis temperature on the chromium concentration of the alkaline hydrolysis solid residues.

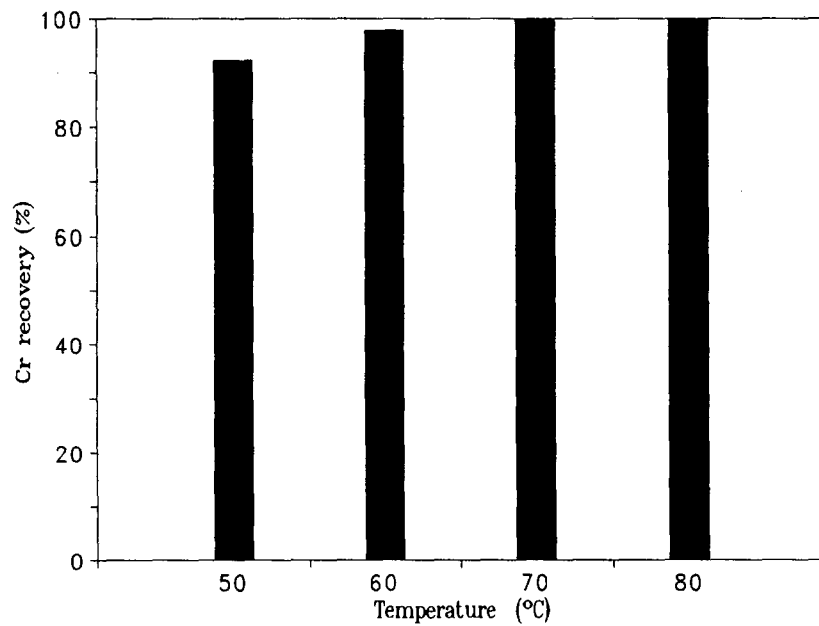


Figure 3.6. Effect of hydrolysis temperature on the post-hydrolysis recovery of chromium.

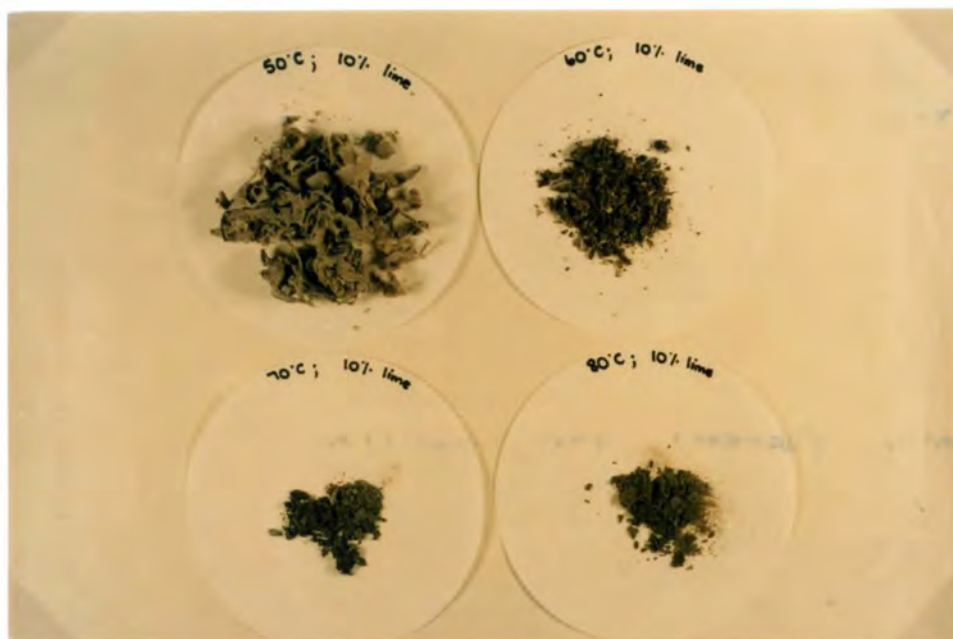


Plate 3.3. Desiccated solid residues of the wet blue shavings hydrolysed in 10% lime solutions at temperatures ranging from 50–80°C.



Plate 3.4. Acid wash supernatants and solid residues of the samples heated over the range 50–80°C.

The bleached appearance of the 50°C residue is clearly evident, confirming the high percentage chromium recovery obtainable after hydrolysis at only 50°C. The acid wash supernatants ranged in colour from pale blue (50°C) to dark blue-green (70 and 80°C). The appearance of the acid washed solid residues was as described for lime (section 2.2.1.3 above).

2.2.3. Hydrolysis period.

The hydrolysis reaction was repeated for periods of 1, 2, 6, 12 and 24 hours. The established optimum concentration of lime (10%) was added to all sample flasks, and the flasks incubated at the established optimum temperature (70°C).

2.2.3.1. Solubilisation of the shavings during alkaline hydrolysis.

The effect of the hydrolysis period on the solubilisation of wet blue shavings is shown in Figure 3.7, together with the percentage chromium recovered from each sample. The initial pH of the hydrolysis media ranged from 10.63–10.84 (Appendix II, Table II). The 34.7% solubilisation of the shavings in the first hour of hydrolysis represented virtually half of the total solubilisation that occurred in the entire 24 hour period (71.5%). This suggests an initial rapid stage in solubilisation. Thereafter, the rate of solubilisation declined, with minimal further solubilisation occurring in the last 18 hours of hydrolysis (6 hours, 64.3% solubilisation vs 24 hours, 71.5% solubilisation). Over 84% of the chromium was, however, recovered after only 1 hour of hydrolysis. This was increased to virtually complete recovery with extension of the hydrolysis period to 12 or 24 hours (100 and 98% recovery respectively).

Examination of the desiccated solid residues remaining after alkaline hydrolysis showed that for hydrolysis periods of 6 hours or less, the material retained the initial ribbon-like structure of the crude shavings. The proportion of fibrous material still evident in the 1–6 hour solid residues (dark green and brittle) decreased proportionately with time. Complete fragmentation of the shavings occurred after 12 hours. The 12 and 24 hour solid residues consisted primarily of a friable, dark green material which, when dry, disintegrated into coarse granules when crushed. No fibrous residue was evident in the 12 and 24 hour samples.

2.2.3.2. Chromium content of the alkaline hydrolysis fractions.

The chromium concentrations of the hydrolysis filtrates and solid residues, shown in Figure 3.8, indicate that the chromium contained within the crude shavings again remained associated with the solid residues for all hydrolysis periods. The hydrolysis filtrates contained low levels of chromium, within the range 0.23–0.38mg.L⁻¹ (filtrate final pH range 9.66–10.51, Appendix II, Table II). The chromium in the solid residues was increasingly concentrated as solubilisation progressed, particularly within the first 12 hours of hydrolysis (3.6–8.0% chromium content). The final 12 hours of hydrolysis further concentrated the chromium to only 8.4% (4.7% of the total concentration within 24 hours). The chromium was concentrated in the solid residues 1.5–3.6 fold (2.3% initial chromium content, Appendix II, Table I).

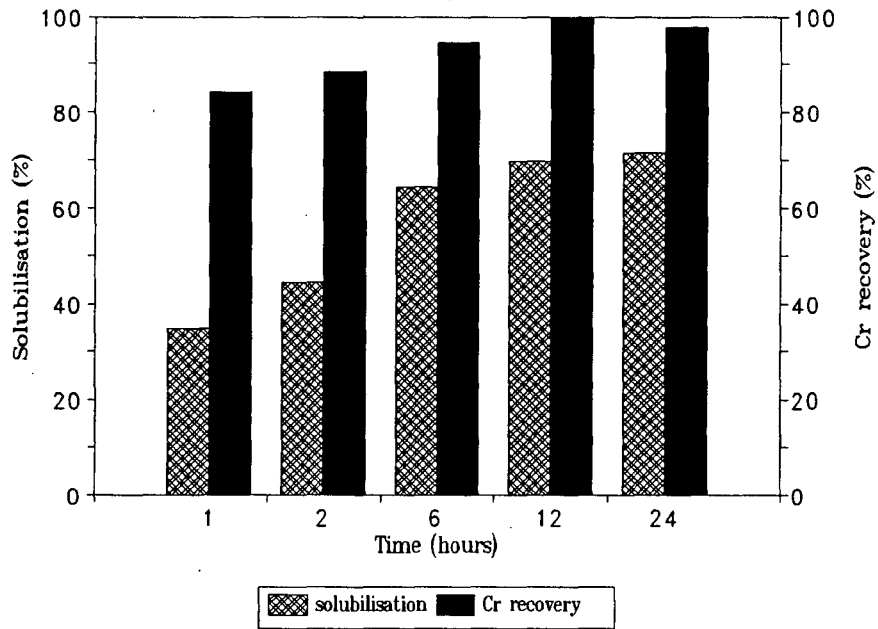


Figure 3.7. Comparison of the effect of hydrolysis period on the solubilisation of wet blue shavings and on chromium recovery.

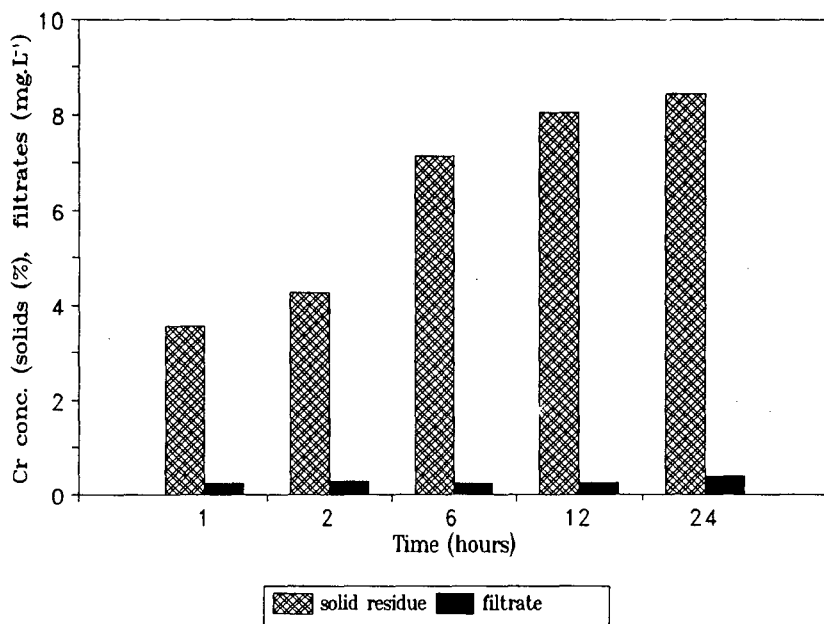


Figure 3.8. Effect of hydrolysis period on the chromium concentrations of the hydrolysis filtrates and solid residues.

2.2.3.3. Chromium recovery by acid wash.

As previously shown in Figure 3.7, over 84% of the chromium was recovered after only 1 hour of alkaline hydrolysis. This increased to essentially complete recovery (100%) after 12 hours. Plate 3.5 shows the acid wash supernatants and solid residues of the 1–24 hour samples. Included for comparison are the acid wash fractions of the crude shavings (effectively zero hour hydrolysis period), referred to as "dry shavings (untreated)". The crude shavings were still blue in colour after acid wash, confirming the very low percentage chromium recovered (24%, section 2.1.2 above). The acid wash supernatant (crude shavings) was a faint blue colour. These were in contrast to the bleached appearance of the 1–24 hour solid residues and the darker colour of their supernatants (pale blue (1 hour)—dark blue-green (12 and 24 hours)).

2.3. Scaled-up investigation.

The optimum conditions of hydrolysis (established to be 10% lime, 70°C and 12 hours) were used to conduct an investigation involving a ten-fold scale-up in both the quantity of wet blue shavings and the volume of water added. In each of the following analyses, the scaled-up sample is compared to the 4g optimisation sample, incubated under identical hydrolysis conditions.

2.3.1. Solubilisation of the shavings during alkaline hydrolysis.

The initial pH of the scaled-up sample's hydrolysis medium was 10.61 (Appendix II, Table II). Figure 3.9 shows that a ten-fold scale-up did not adversely affect the efficiency of the solubilisation process. Solubilisation of the order of 70.0% was recorded for the scaled-up investigation, compared to 69.8% for the 4g optimisation sample (see also Figure 3.7). The macrostructure of the crude shavings (scaled-up sample) was completely degraded to a dark green, fragmented residue which, when dry, was brittle, disintegrating into coarse granules when crushed.

2.3.2. Chromium content of the alkaline hydrolysis fractions.

Under scaled-up conditions, the chromium was still apportioned to the solid residue as shown in Figure 3.10. The scaled-up sample hydrolysis filtrate (final pH 9.85, Appendix II, Table II) contained 0.23mg.L⁻¹ chromium. The chromium associated with the solid residue of the same study was concentrated 3.5 times during solubilisation (8.1% chromium vs 2.3% initial chromium, Appendix II, Table I). Under identical hydrolysis conditions in the 4g analysis, the hydrolysis filtrate contained 0.25mg.L⁻¹ chromium and the solid residue 8.0% chromium (see Figure 3.8).

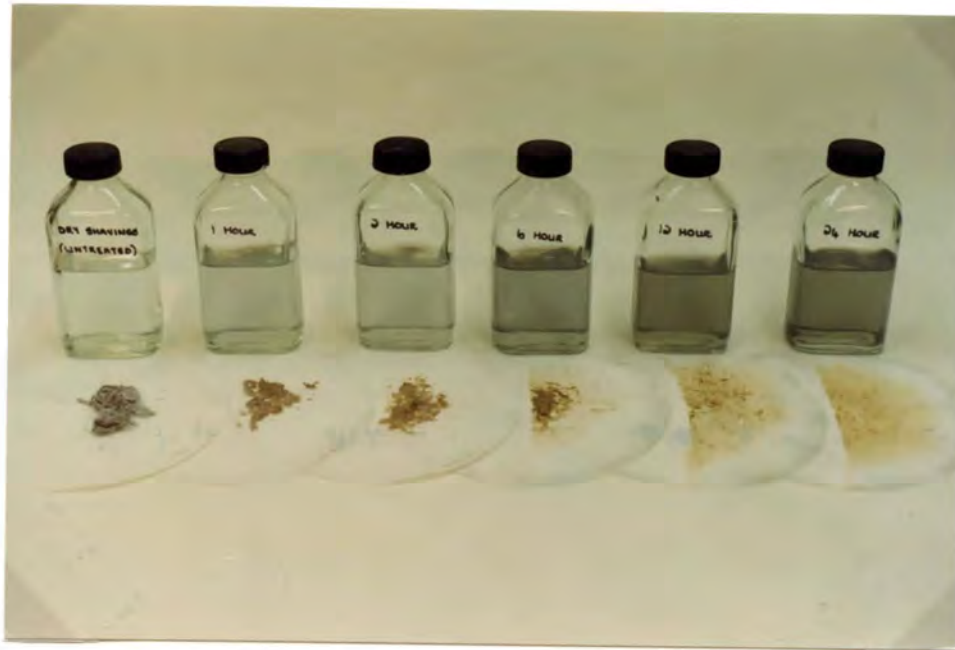


Plate 3.5. Acid wash supernatants and solid residues of the 0–24 hour hydrolysis period study.

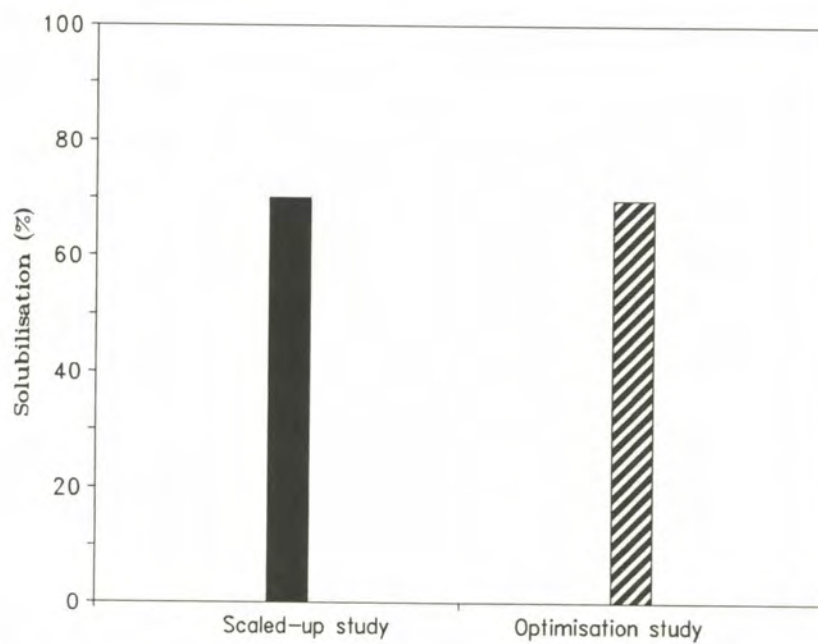


Figure 3.9. Comparison of the solubilisation attained in the 40g (scaled-up) and 4g (optimisation) investigations.

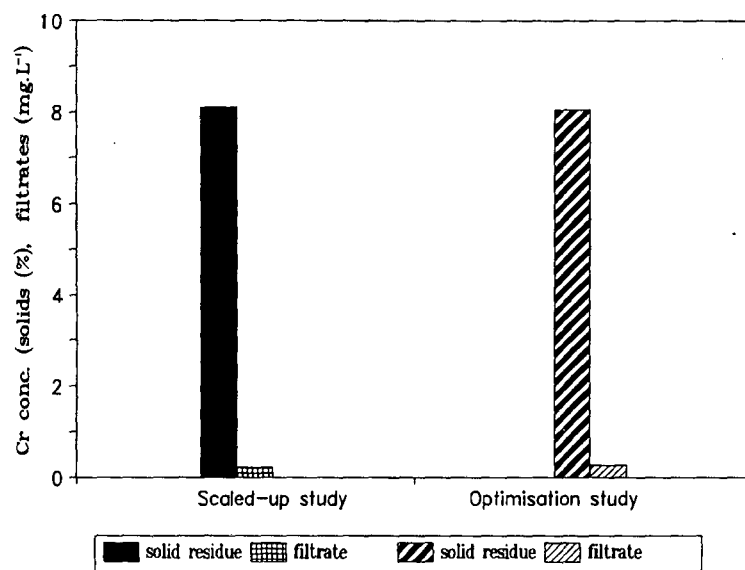


Figure 3.10. Comparative chromium concentrations of the 40g (scaled-up) and 4g (optimisation) alkaline hydrolysis fractions.

2.3.3. Chromium recovery by acid wash.

As shown in Figure 3.11, 98% of the chromium was recovered from the scaled-up sample, compared to 100% from the 4g sample under identical hydrolysis conditions (see also Figure 3.7). The acidic supernatant (scaled-up sample) was dark blue-green in colour, the solid residue a yellow colour.

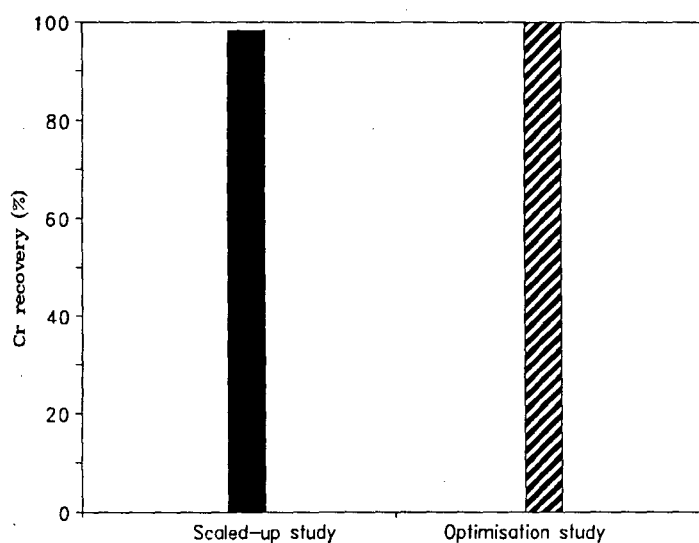


Figure 3.11. Comparative chromium recoveries from the 40g (scaled-up) and 4g (optimisation) investigations.

3. Discussion.

3.1. Hydrolysis of the shavings under alkaline conditions.

The preliminary investigation described in this chapter confirms previous reports in literature that chrome-tanned wet blue shavings can be solubilised under heated alkaline conditions and the chromium removed as an insoluble precipitate (Taylor *et al*, 1990; Alves dos Reis and Beleza, 1991a). The dissociation of the chromium from the protein substrate of the shavings (detanning) and the formation of separate protein and chromium products involved the interaction of two chemical processes, *viz.* the susceptibility of protein to hydrolysis under hot, alkaline conditions (Alves dos Reis and Beleza, 1991a), and the ability of trivalent chromium to precipitate as an insoluble residue in a pH environment above 4 (Thorstensen, 1993). This precipitate is known to consist almost entirely of chromium hydroxide (Thorstensen, 1993) and in consequence was not analysed further in this study. The mechanism of lime-induced solubilisation of the protein and the formation of the chromium precipitate will be discussed in greater detail in Chapter 6.

The low concentrations of chromium solubilised during the detanning process, shown in these investigations to be less than 0.5mg.L^{-1} , complies with South African legal discharge limits for total chromium in effluents (Rawlings *et al*, 1987). This is important if this process is to be included in a treatment programme for tannery solid wastes. It is significant that the generation of a waste medium, itself dependent on further treatment to remove the chromium, be avoided since this would increase the overall cost of a treatment process.

The use of calcium hydroxide (Ca(OH)_2) for the provision of an alkaline environment, resulted in the formation of a chromium precipitate which displayed settling characteristics conducive to isolation by simple filtration or settling under the action of gravity. This attribute was considered important since fine filtration is costly on an industrial scale.

3.2. Recovery of the precipitated chromium hydroxide by acid wash.

The resolubilisation of the precipitated chromium hydroxide during acid wash employed the inverse of the chemical principle utilised in alkaline hydrolysis. Whereas above pH 4 chromium precipitates as a hydroxide, at a pH below 4 the chromium is converted to a soluble form, *viz.* chromium sulphate, following the addition of H_2SO_4 (Thorstensen, 1993). This enables the chromium to be leached from the solid precipitate produced during alkaline hydrolysis and recovered as a potentially reusable stock of chromium.

The ability of protein to solubilise under acidic conditions as well (Alves dos Reis and Beleza, 1991a), and thereby to contaminate the solubilised chromium, was discouraged by the absence of any artificial heat source during the acid wash procedure. This resulted in most of the protein

residue remaining as a chrome-free solid residue after the acid wash procedure. Too high a concentration of protein in the solubilised chromium extract may have a deleterious effect on subsequent leather quality where the recovered chromium is used to tan hides (Russell, 1993). The observed high chromium recovery where the extent of protein solubilisation obtained during hydrolysis was still low, suggests that the chromium was precipitated from the shavings before an advanced stage of solubilisation was attained. In this regard it would appear that the shavings were readily detanned, provided alkaline conditions (i.e. a hydroxide reserve) were present during hydrolysis to precipitate the chromium. It is suggested that this could be due to the higher susceptibility of the protein-chromium bond to cleavage, as opposed to the more resistant peptide bond. This will be discussed in Chapter 6.

3.3. Effect of preceding alkaline hydrolysis on chromium recovery.

This preliminary investigation demonstrated that the inclusion of a hydrolytic stage prior to acid washing had a marked effect on the recovery of chromium. The approximately two-fold increase in recovery observed following simple, non-alkaline hydrolysis was increased to a four-fold recovery when hydrolysis was conducted under alkaline conditions. These results suggest that the hydroxide ion concentration present in the approximately neutral water medium (0% lime sample) was of sufficient concentration to enable limited precipitation of the chromium hydroxide. The significantly higher hydroxide concentrations provided by the alkaline conditions further promoted the precipitation process, hence the observed improved chromium recovery.

3.4. Optimum hydrolysis conditions.

These investigations clearly indicate that optimisation of the hydrolysis conditions affected solubilisation of the shavings to a far greater extent than chromium recovery. This is assumed to be due to the recovery of chromium being dependent only on the provision of alkaline conditions during hydrolysis, to enable generation of the chromium precipitate for later resolubilisation.

The variables optimised in this study (i.e. lime concentration, hydrolysis temperature and hydrolysis period) are discussed individually below. Reference is made to the similar optimisation studies undertaken by Taylor *et al* (1990) and Alves dos Reis and Beleza (1991a). Both studies involved the use of chrome shavings as the solid material, the only difference between the two studies being the inclusion of a proteolytic enzyme by Taylor *et al* (1990) to enhance the solubilisation process. The hydrolysis conditions of Taylor's study were therefore optimised in accordance with the optimum activity of the enzyme.

3.4.1. Lime concentration.

That the addition of lime significantly enhanced solubilisation only when lime in excess of 6% was added (Figure 3.1), suggests that it was not only the provision of alkaline conditions that was necessary for solubilisation to occur, but that there existed a threshold concentration of hydroxide necessary for enhanced solubilisation. From this investigation it would appear to correlate with a pH above 11.17 (Figure 3.1). Assuming that the protein-chromium bond is hydrolysed first, the hydroxide would initially be consumed in detanning, with less hydroxide available for interaction with the amide bonds. Since only a finite concentration of lime can be dissolved at a given time (lime saturated solution), higher concentrations of lime would enable the establishment of a lime reserve, representing the lime not yet dissolved. This lime reserve would have replenished the hydroxide as it was consumed, allowing for prolonged interaction with the amide bonds, and therefore increased solubilisation. This proposed buffering action of lime is supported by the observed smaller pH changes during hydrolysis with increased concentrations of lime added (Appendix II, Table II).

In this investigation the concentration of lime for optimum solubilisation was found to be 10% (Figure 3.1). This compares favourably with the similar optimisation study of Alves dos Reis and Beleza (1991a), viz. 8–10% lime. An optimum lime concentration of 6% was reported by Taylor *et al* (1990). This lower concentration was selected in accordance with the optimum pH conditions for the proteolytic enzyme used.

The comparable chromium recovery for the 4–12% lime samples seen in this study (Figure 3.3), affords the opportunity to select hydrolysis conditions conducive to chromium recovery, but at the expense of solubilisation. Since the objective of this study was to optimise both chromium recovery and solubilisation, the higher lime concentration of 10% was selected for further studies, but it must be stressed that should detanning be the sole objective, a far lower lime concentration of 4% is sufficient.

3.4.2. Hydrolysis temperature.

Alves dos Reis and Beleza (1991a) considered the hydrolysis temperature to be perhaps the most important factor in the production of a protein concentrate free of chromium, but this investigation found very little influence of temperature on chromium solubilisation, at least within the 50–80°C temperature range (Figure 3.4). What was conclusively shown, however, was the significant effect of the hydrolysis temperature on protein solubilisation (Figure 3.4). In fact, the selection of an adequate hydrolysis temperature actually appeared to be of greater significance to solubilisation than the provision of optimum alkaline conditions. This is shown by the higher (1.5

times) solubilisation of the 0% lime sample incubated at 65°C, than the 10% lime sample (i.e. optimum lime concentration) incubated at 50°C (Figures 3.1 and 3.4 respectively). Understandably, an increase in the hydrolysis temperature will favour hydrolysis kinetics.

In this investigation the optimum hydrolysis temperature for solubilisation was found to be 70°C (Figure 3.4). This is approximately mid-way between the optimum temperatures established by Taylor *et al* (1990), viz. 60–65°C, and Alves dos Reis and Beleza (1991a), viz. 80 or 90°C. The very similar chromium recoveries of the 50–80°C samples obtained in this study (Figure 3.6), again offers the opportunity to operate the alkaline hydrolysis process at the lower temperature of 50°C, opportune if chromium recovery is the sole objective. Notwithstanding the associated cost saving in heating that this would represent, the higher hydrolysis temperature of 70°C was still selected for further studies, in order to satisfy the dual purposes of chromium recovery and protein solubilisation optimisation.

3.4.3. Hydrolysis period.

Likewise, the hydrolysis period can also be tailored to suit chromium recovery and/or protein solubilisation. While the majority of the chromium was recoverable after only one hour of hydrolysis, longer incubation periods were necessary to enable optimum protein solubilisation (Figure 3.7). The hydrolysis period for optimum protein solubilisation was found to be 12 hours, selected on the assumption that the marginal increase in solubilisation for longer hydrolysis periods (i.e. from 12–24 hours) would not prove to be cost-effective. The same argument can also hold true for the very small increase in protein solubilisation obtained from 6 to 12 hours but, in order to optimise the solubilisation effect, the longer hydrolysis period (12 hours) was selected and the heating cost overlooked. The levelling off in solubilisation with longer hydrolysis periods (Figure 3.7) is assumed to be a consequence of the hydrolysis medium approaching protein-saturation point from the solubilised protein content, since the final pH of the medium was still high (Appendix II Table II).

By comparison, the optimum hydrolysis periods established by Taylor *et al* (1990) (30 minutes), and Alves dos Reis and Beleza (1991a) (30–45 minutes), were considerably shorter. A cost/benefit analysis would be required to establish whether the cost of the proteolytic enzyme (Taylor *et al*, 1990) or the high hydrolysis temperatures (80–90°C, Alves dos Reis and Beleza, 1991a) outweigh the findings of this investigation.

Two further variables not optimised in this preliminary investigation but which, given an overview of the results obtained, would undoubtedly have influenced solubilisation more than chromium recovery, are the size of the shavings and the proportion of shavings to water.

The ratio of shavings to water will hereafter be referred to as the loading ratio. Alves dos Reis and Beleza (1991a) established that the absolute maximum ratio of water to blue shavings should not exceed 10:1, since the volume of water that must be evaporated to dry the residue will contribute significantly to the cost of the process. The proportion of water to shavings utilised in this investigation represented a loading ratio of 75:1 (water:shavings). The effect of an approximate 10:1 loading ratio of medium:shavings on solubilisation is demonstrated in Chapter 5 and the validity of this loading ratio is discussed in Chapter 6. The size of the shavings is reported to have a small influence on the reaction rate (Alves dos Reis and Beleza, 1991b).

3.5. Scaled-up investigation.

A comparison of the results obtained for the scaled-up investigation (40g shavings) and the smaller hydrolysis optimisation investigation (4g shavings), conducted under identical hydrolysis conditions, showed that a ten-fold scale-up did not decrease the capacity of the alkaline hydrolysis process to solubilise protein, nor the extent of chromium recovery. Since this scaled-up investigation involved a proportionate scale-up in the quantity of shavings and medium, the loading ratio remained 75:1 (water:shavings). These results suggest potential for application of this treatment process in an industrial pilot-scale study.

4. Conclusion.

1. Wet blue shavings can be separated into a protein component (solubilised and unsolubilised) and an insoluble chromium precipitate, following hydrolysis under heated alkaline conditions.
2. The protein-containing supernatant contained less than 0.5mg.L^{-1} chromium.
3. The precipitated chromium hydroxide was recovered by conversion to soluble chromium sulphate, following leaching of the chromium-containing solid residue with dilute H_2SO_4 .
4. The optimum conditions of hydrolysis, established to maximise both chromium recovery and solubilisation of the shavings, were: 10% lime (degree of alkalinity), 70°C (hydrolysis temperature) and 12 hours (hydrolysis period). However, less extreme hydrolysis conditions are sufficient for chromium recovery at the expense of protein solubilisation.
5. Chromium recovery was unaffected by variation of the hydrolysis conditions, instead it appeared dependent only on the provision of alkaline conditions during hydrolysis.
6. A ten-fold scale-up did not reduce the capacity of the alkaline hydrolysis process to solubilise the shavings, nor did it decrease the percentage recovery of the chromium.

CHAPTER 4

ALKALINE TANNERY EFFLUENTS AS HYDROLYSIS MEDIA

1. Introduction.

Once the preliminary investigation had confirmed that wet blue shavings could be detanned under simulated alkaline conditions (Chapter 3), attention was then focused on whether the highly alkaline beamhouse effluents could be used as substitute hydrolytic media. This would enable use to be made of the residual alkalinity of the effluents to provide the required alkaline conditions for hydrolysis.

The beamhouse effluents, produced during the preparation of the hides for tanning, collectively refer to those effluents produced up to, but excluding, the pickling stage of leather manufacture (refer to Figure 1.1). As a result of the variety of processes involved in the beamhouse operations, not all of the effluents produced are highly alkaline. Two stages of the process do, however, generate notably alkaline effluents, namely the liming and the unhairing stages. The large quantities of lime ($\text{Ca}(\text{OH})_2$) added to the hides during these processes account for the high alkalinity of the effluents discharged (Collivignarelli and Barducci, 1984).

Three separate effluents were considered as alternative alkaline media: the unhairing effluent, the unhairing wash effluent (referred to as the wash effluent) and a combined effluent stream. The combined effluent consisted of a combination of the liming, lime wash, unhairing and unhairing wash streams. The first investigation assessed the relative effectiveness of the individual process effluents (unhairing and wash effluents) as hydrolytic media for treating wet blue shavings, the batch-like nature of the tanning process enabling collection of these effluents as discrete streams (Kumar, 1983). Only the hydrolysis temperature and hydrolysis period were varied to establish the optimum conditions for each effluent, the conditions again selected to favour solubilisation of the shavings and chromium recovery. A scaled-up investigation was conducted using the established superior individual process effluent and the optimised hydrolysis conditions. A second scaled-up investigation examined the effectiveness of the combined effluent as a potential hydrolysis medium. This investigation was prompted by the current tendency of many tanneries to combine the various alkaline effluent streams for subsequent treatment. The established optimum conditions of the scaled-up individual process effluent study were adopted for use in the combined effluent study.

2. Results.

Chemical profiles of the unhairing effluent, wash effluent and combined effluent are shown in Table 4.1.

Table 4.1. Chemical profiles of the unhairing, wash and combined effluents.

	unhairing effluent	wash effluent	combined effluent
pH	12.38	12.20	12.05
conductivity (mS.m ⁻¹)	4 270	1 490	4 703
alkalinity - phenolphthalein (mg.L ⁻¹)	4 542	1 622	1 785
- methyl orange (mg.L ⁻¹)	11 171	3 253	3 915
PV (mg.L ⁻¹)	8 989	1 995	2 982
COD (mg.L ⁻¹)	33 053	5 451	10 676
ammonia (mg.L ⁻¹)	1 627	170	380
nitrate (mg.L ⁻¹)	427	114	193
TKN (mg.L ⁻¹)	5 591	621	1 363
sodium (mg.L ⁻¹)	2 080	1 850	17 700
calcium (mg.L ⁻¹)	920	440	720
sulphate (mg.L ⁻¹)	1 759	307	513
sulphide (mg.L ⁻¹)	8 522	1 674	1 885
chloride (mg.L ⁻¹)	11 613	2 961	18 099
chromium (mg.L ⁻¹)	0.19	0.16	1.02
fat, oil or grease (mg.L ⁻¹)	240	89	123
settling rate	658mL in 2 hours	138mL in 2 hours	48mL in 2 hours

The considerably higher quantity of suspended material present in the unhairing effluent, together with the requirement for a reasonably clarified effluent for use in hydrolysis, necessitated examination of an extended settling time for this effluent. Figure 4.1 shows the settling of the unhairing effluent over 48 hours. The wash and combined effluents are included for comparison.

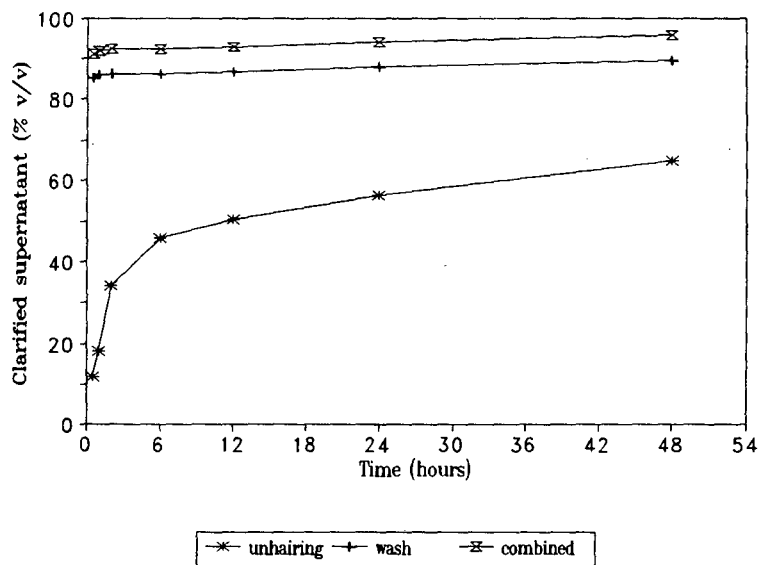


Figure 4.1. Settling profiles of the unhairing, wash and combined effluents over 48 hours.

It is evident from Figure 4.1 that a minimum of 6 hours was required to produce a reasonably clarified unhairing effluent for use in hydrolysis (46% by volume clarified). Thereafter, the precipitated material continued to compact, as shown by the gradual increase in the volume of clarified effluent. The wash and combined effluents required less than 30 minutes for good clarification (0–30 minutes settling not shown in Figure 4.1). Visible settling was complete within only three minutes (wash effluent) and two minutes (combined effluent).

2.1. Optimum conditions for alkaline hydrolysis.

The optimum conditions for alkaline hydrolysis were established only for the unhairing and the wash effluents. Where possible, the two effluents are presented together for comparison.

2.1.1. Hydrolysis temperature.

The hydrolysis reaction was repeated over the temperature range 50–80°C, in ten degree increments of temperature. The guideline hydrolysis period (12 hours) was selected on the basis of the findings in Chapter 3.

2.1.1.1. Solubilisation of the shavings during alkaline hydrolysis.

The effect of hydrolysis temperature on the solubilisation of the shavings is shown in Figure 4.2. As occurred with the addition of lime to the shavings (Chapter 3), the dissolved and/or suspended materials in the effluents contributed to the weight of the solid residues obtained.

The excess weight was corrected for by means of control samples (equivalent volume of effluent alone), incubated in an identical manner to the sample flasks. The same correction procedure was followed throughout Chapter 4.

Figure 4.2 shows that significantly higher solubilisation was attained in the wash effluent samples, with up to 61.3% solubilisation compared to a maximum of 44.7% solubilisation in the unhairing effluent. The initial pH's recorded for all samples (controls included) ranged between 11.20 and 11.85 (Appendix II, Tables III and IV). Increasing the hydrolysis temperature from 50–80°C did not enhance solubilisation in the unhairing effluent samples. Solubilisation actually decreased between 70 and 80°C. Maximum increase in solubilisation of the wash effluent samples occurred between 50 and 70°C (7.2 fold increase, 8.4% vs 60.9% solubilisation). Little further improvement in solubilisation occurred for the 80°C wash effluent sample (61.3% solubilisation).

Despite the limited solubilisation of the unhairing effluent samples, the solid residues all indicated complete breakdown in physical structure. This is shown in Plate 4.1. Only friable fragments of the crude shavings remained, which disintegrated into coarse granules (50°C), through to a fine silt-like material (80°C), when crushed. The desiccated solid residues of the wash effluent samples (Plate 4.2) did not show the same complete breakdown in physical structure. The shavings hydrolysed at 50°C (low solubilisation) still closely resembled the crude shavings in colour and structure. The 60–80°C residues were fragmented, but were not as finely divided as the unhairing effluent samples.

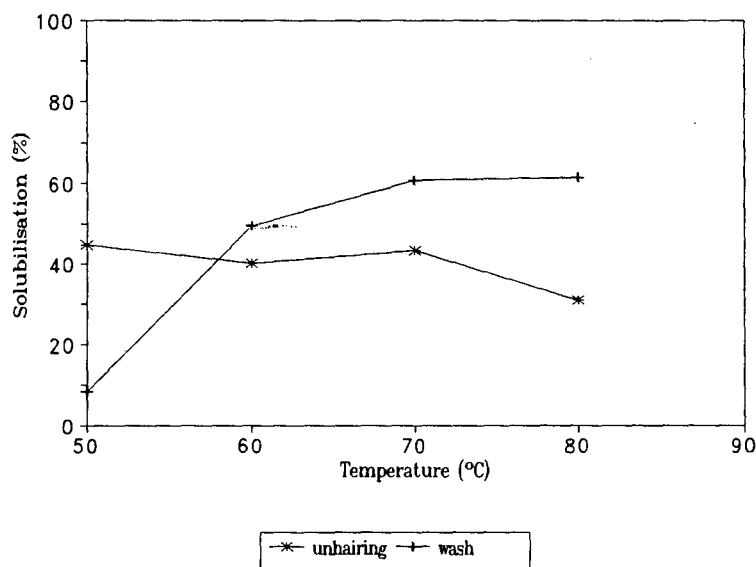


Figure 4.2. Effect of hydrolysis temperature on the solubilisation of wet blue shavings in the unhairing and wash effluents.

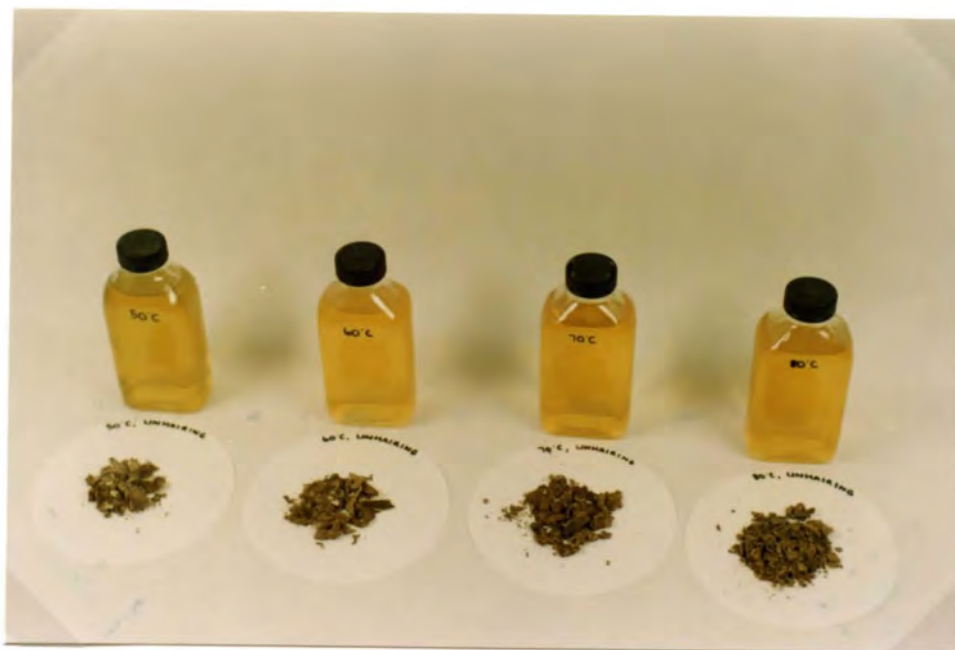


Plate 4.1. Desiccated solid residues of the shavings hydrolysed at 50–80°C in the unhairing effluent.

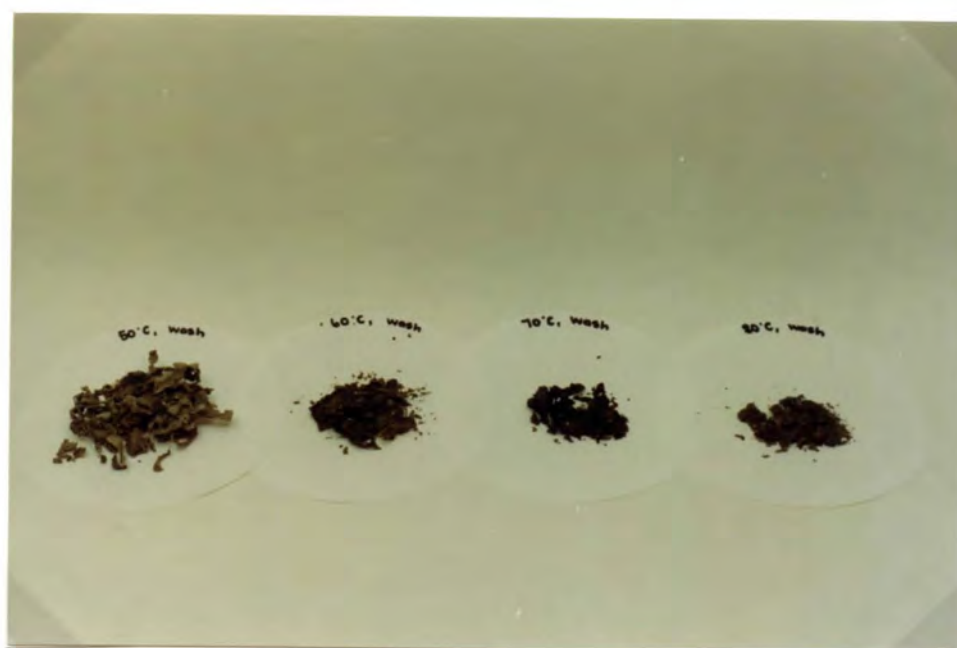


Plate 4.2. Desiccated solid residues of the shavings hydrolysed at 50–80°C in the wash effluent.

2.1.1.2. Chromium content of the alkaline hydrolysis fractions.

Figures 4.3 and 4.4 show the apportionment of chromium during the unhairing and wash effluent hydrolyses respectively. The filtrate chromium concentrations reflect the nett chromium solubilised from the shavings during hydrolysis.

Both effluent investigations were characterised by low concentrations of solubilised chromium ($0.16\text{--}0.26\text{mg.L}^{-1}$ unhairing effluent, $0.03\text{--}0.51\text{mg.L}^{-1}$ wash effluent). This indicated that the chromium was still apportioned to the solid residues during hydrolysis. While an increase in the hydrolysis temperature did not cause a corresponding increase in solubilised chromium in the unhairing effluent filtrates, the higher chromium concentrations of the 50 and 60°C wash effluent filtrates (0.49 and 0.51mg.L^{-1} chromium) suggest a possible influence of temperature on chromium solubilisation. The pale blue tint observed in the otherwise yellow wash effluent filtrates (50 and 60°C), substantiates the higher chromium concentrations. The colour and final pH ranges of the unhairing and wash effluent filtrates are presented in Table 4.2. The chromium in the solid residues was concentrated $1.3\text{--}1.7$ fold in the unhairing effluent samples and $1.0\text{--}2.8$ fold in the wash effluent samples (initial chromium content 1.9% unhairing effluent, 2.4% wash effluent, Appendix II Table I).

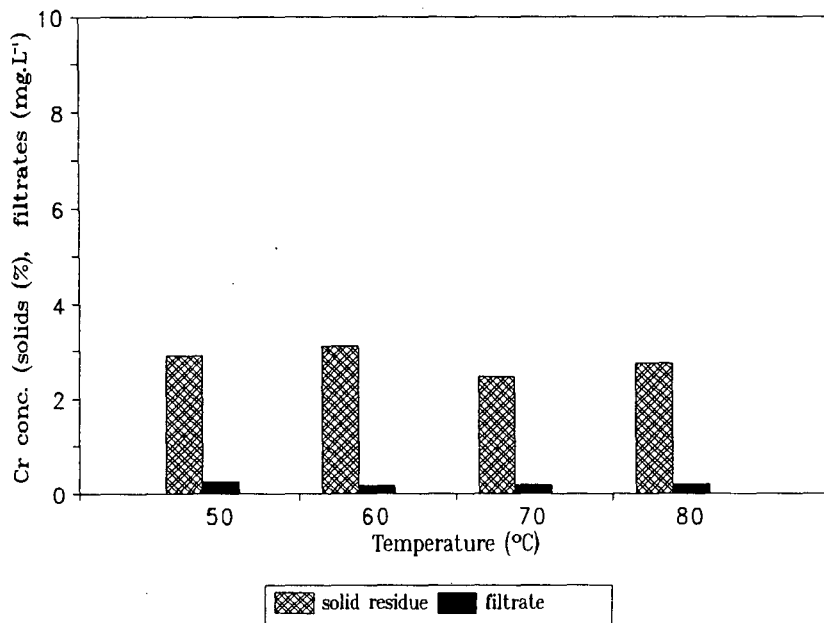


Figure 4.3. Effect of hydrolysis temperature on the chromium concentrations of the unhairing effluent filtrates and solid residues.

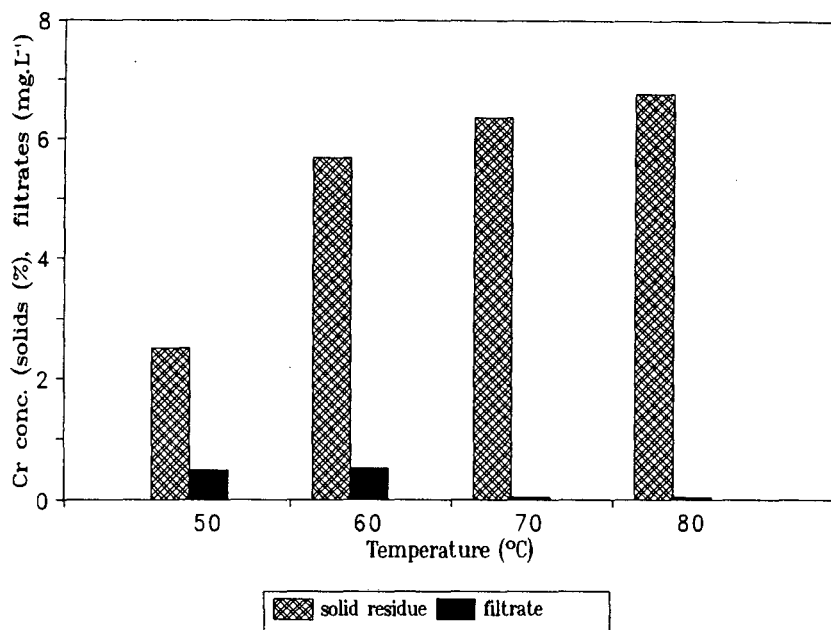


Figure 4.4. Effect of hydrolysis temperature on the chromium concentrations of the wash effluent filtrates and solid residues.

Table 4.2. Colour and final pH ranges of the 50–80°C unhairing and wash effluent hydrolysis filtrates.

	sample filtrates	control filtrates
unhairing effluent	dark yellow (50–80°C) pH 10.37–11.59	yellow-brown (50, 60°C) – dark yellow (70, 80°C) pH 10.87–11.74
wash effluent	pale yellow (50–80°C) with blue tint (50, 60°C) pH 9.80–11.04	pale yellow (50–80°C) but slightly darker than sample filtrates pH 10.99–11.72

2.1.1.3. Chromium recovery by acid wash.

It is evident from Figure 4.5 that, in general, slightly more chromium was recovered from the wash effluent samples (92–100%) compared to the unhairing effluent samples (74–95%). Chromium recovery did not appear to be significantly influenced by temperature variation in either study. In addition, despite differences in the extent of solubilisation attained for the two effluents (Figure 4.2), recovery of the chromium was essentially comparable, suggesting that chromium recovery is also independent of the degree of solubilisation attained during alkaline hydrolysis. This is strongly suggested by the essentially complete recovery of the chromium (100%) from the 50°C wash effluent sample, where only 8.4% solubilisation (Figure 4.2) was recorded.

Plates 4.3 (unhairing effluent) and 4.4 (wash effluent) confirm visually that the shavings were detanned with use of the alkaline effluents during hydrolysis. The bluish colour of all the acid wash supernatants signified the presence of chromium in solution, and the bleached appearance of the 50°C, and to a lesser extent the 60°C, wash effluent solid residues (Plate 4.4) provided further evidence to the fact. The brown colour of the remaining solid residues unfortunately masked any bleached appearance.

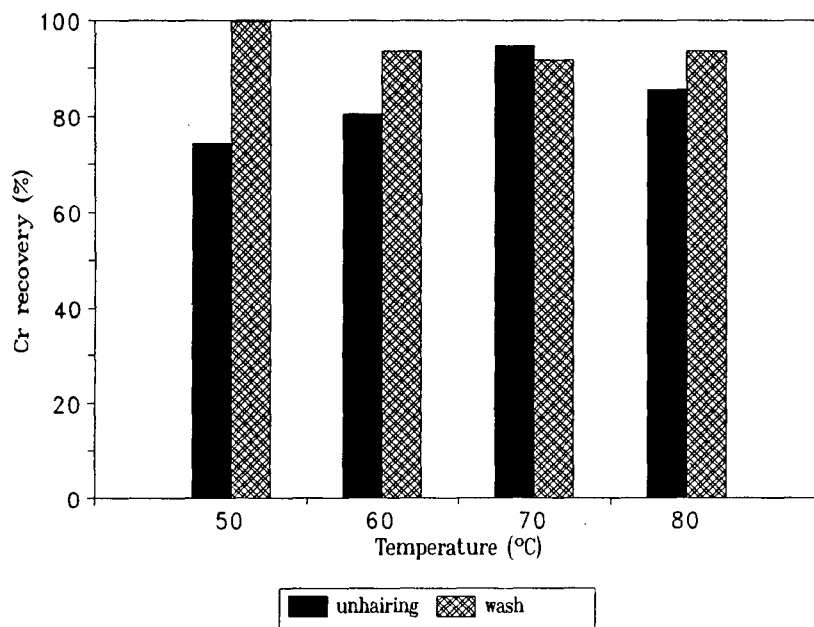


Figure 4.5. Comparison of the chromium recoveries of the 50–80°C unhairing and wash effluent samples.



Plate 4.3. Acid wash supernatants and solid residues of the 50–80°C unhairing effluent samples.

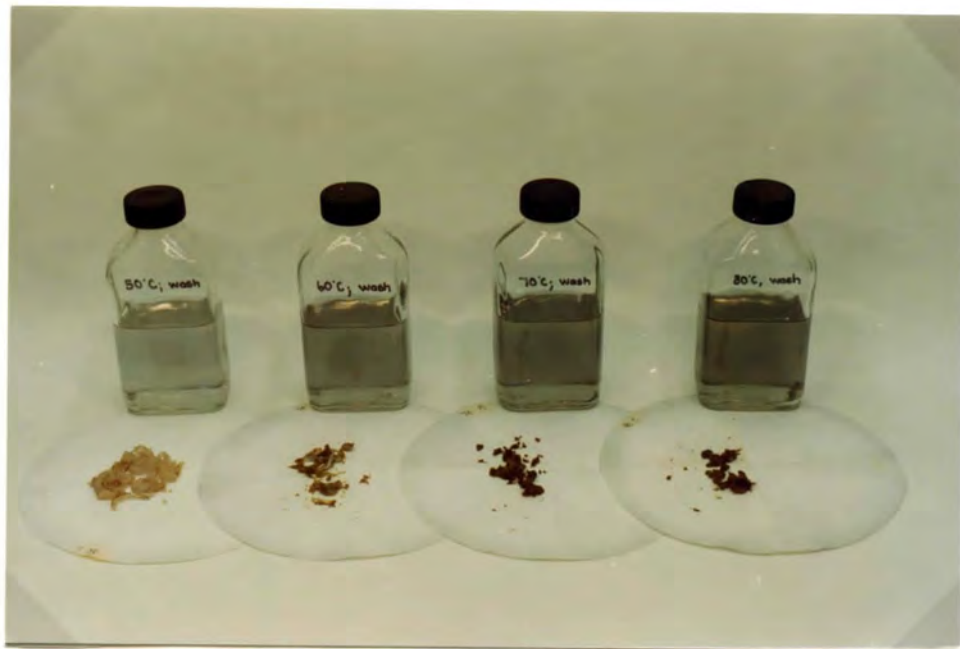


Plate 4.4. Acid wash supernatants and solid residues of the 50–80°C wash effluent samples.

2.1.2. Hydrolysis period.

The hydrolysis reaction was repeated for periods of 1, 2, 6, 12 and 24 hours. The established optimum temperature of the wash effluent analysis (70°C) was used for both studies.

2.1.2.1. Solubilisation of the shavings during alkaline hydrolysis.

The effect of the hydrolysis period on the solubilisation of the shavings is shown in Figure 4.6. The initial pH's recorded for all samples (controls included) ranged between 11.30 and 11.66 (Appendix II, Tables III and IV). Solubilisation of the unhairing effluent samples showed some measure of dependence on hydrolysis period during the first 6 hours of hydrolysis, increasing from 26.9% (1 hour) to 66.1% (6 hours). Thereafter, an apparent decrease in solubilisation occurred (58.4 and 44.1% solubilisation for 12 and 24 hours respectively). The overall degree of solubilisation was, however, higher than that recorded for temperature studies with this effluent (Figure 4.2). A more uniform solubilisation profile was obtained for the wash effluent. The 32.9% solubilisation recorded within the first hour of hydrolysis increased to 53.4% solubilisation (6 hours). Marginal improvement in solubilisation occurred during the last 18 hours of hydrolysis (3.8% of total solubilisation).

Examination of the desiccated solid residues showed that the shavings incubated in the unhairing effluent had fragmented into smaller pieces within the first hour of hydrolysis, the size of the fragments decreasing as hydrolysis progressed. These solid residues were all brown in colour and friable after only 1 hour of hydrolysis, disintegrating into coarse granules (1 hour) through to a fine silt-like material (24 hours) when crushed. No fibrous residue was evident after the first hour of hydrolysis. Conversely, the wash effluent solid residues remained as thin strands of partly digested shavings for the first 2 hours of hydrolysis and thereafter as fragments of the crude shavings, which progressively decreased in size with a longer hydrolysis period. The fibrous residue was no longer evident by 6 hours of hydrolysis. All wash effluent solid residues were green in colour.

2.1.2.2. Chromium content of the alkaline hydrolysis fractions.

The chromium concentrations of the hydrolysis filtrates (nett chromium solubilised) and the solid residues are compared in Figures 4.7 and 4.8 for the unhairing and wash effluents respectively. The colour and final pH ranges of the sample and control filtrates are shown in Table 4.3.

Chromium concentrations greater than 0.5mg.L⁻¹ were recorded in the filtrates for the first hour (unhairing effluent) and the first two hours (wash effluent), but declined rapidly thereafter to below 0.4mg.L⁻¹. The chromium apportioned to the solid residues was concentrated 1.9–2.1 fold (unhairing effluent) and 1.9–2.2 fold (wash effluent). The initial chromium content of the shavings was 1.6% (unhairing effluent) and 2.4% (wash effluent) (Appendix II Table I).

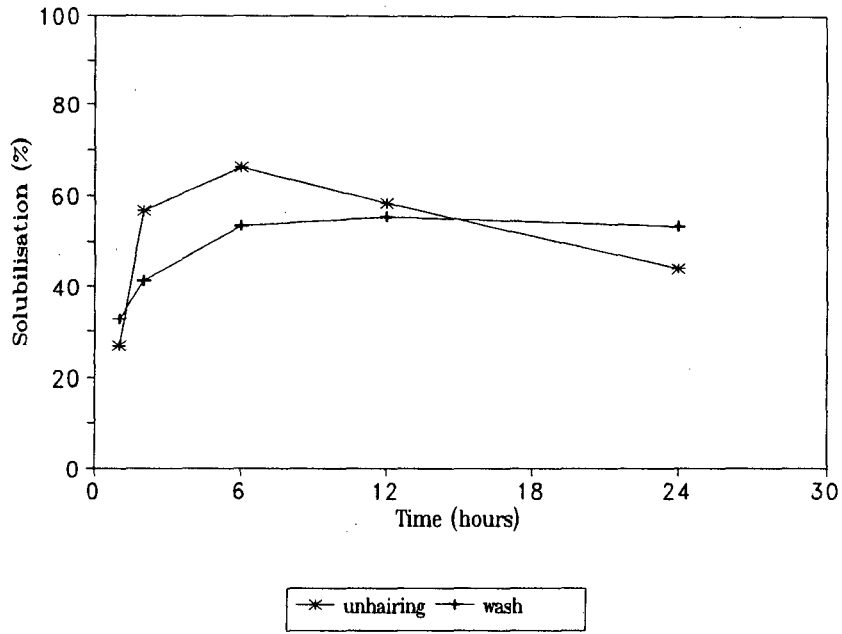


Figure 4.6. Effect of hydrolysis period on the solubilisation of wet blue shavings in the unhairing and wash effluents.

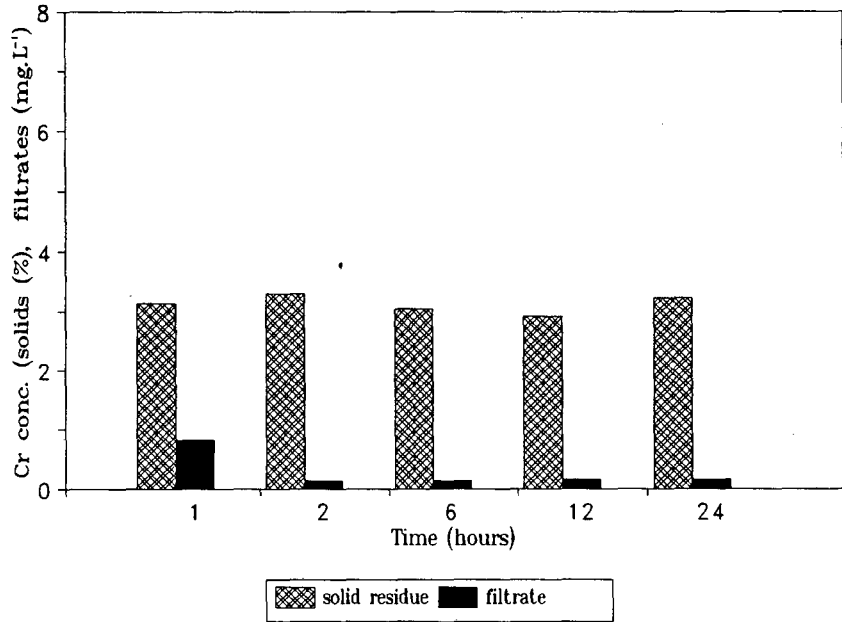


Figure 4.7. Effect of hydrolysis period on the chromium concentrations of the unhairing effluent hydrolysis filtrates and solid residues.

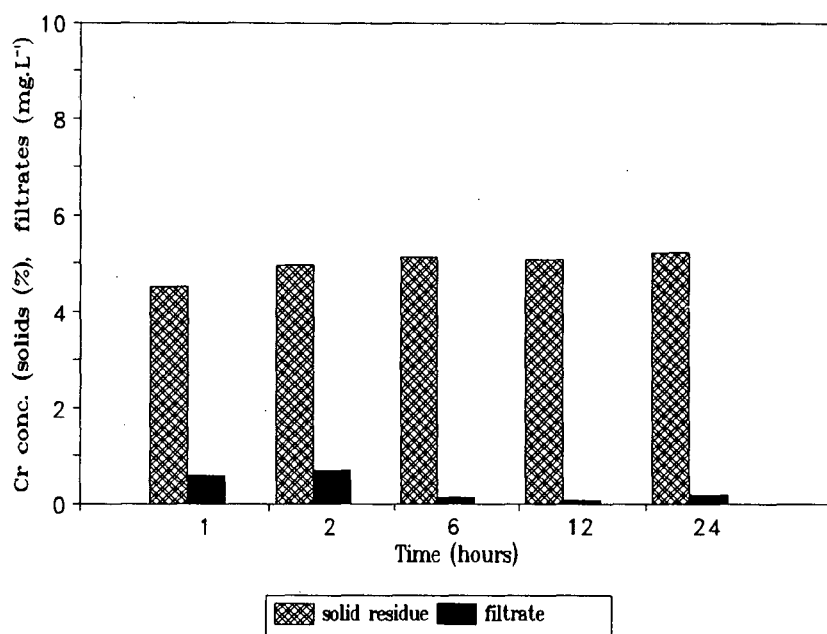


Figure 4.8. Effect of hydrolysis period on the chromium concentrations of the wash effluent hydrolysis filtrates and solid residues.

Table 4.3. Colour and final pH ranges of the 1–24 hour unhairing and wash effluent hydrolysis filtrates.

	sample filtrates	control filtrates
unhairing effluent	green-white (1 hour) – dark yellow (6–24 hours) pH 10.42–11.25	dark green (1 hour) – orange-brown (12, 24 hours) pH 10.89–11.38
wash effluent	yellow-white (1 hour) – darker yellow (12, 24 hours) pH 10.92–11.88	yellow-green (1, 2 hours) – yellow-brown (12, 24 hours) pH 11.16–11.50

2.1.2.3. Chromium recovery by acid wash.

Figure 4.9 shows that marginally higher levels of chromium were recovered from the solid residues of the shavings hydrolysed in the wash effluent. Between 82 and 89% of the chromium was recovered from the wash effluent samples, compared to 66–85% from the unhairing effluent samples. Comparable chromium recoveries were evident for all hydrolysis periods within each effluent investigation. This is especially evident in the wash effluent samples where 84% of the chromium was recovered after only 1 hour, with no further increase evident after 24 hours.

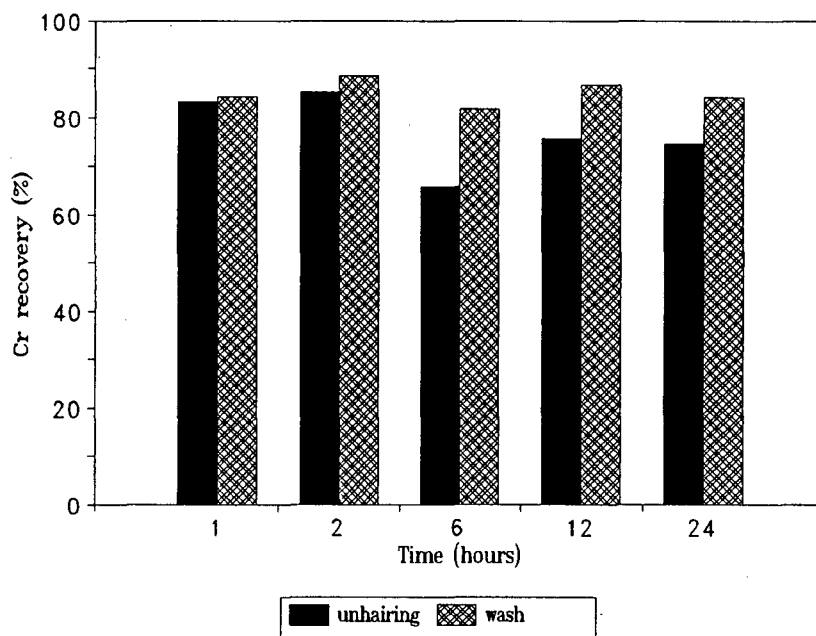


Figure 4.9. Comparison of the recovery of chromium from the 1–24 hour unhairing and wash effluent investigations.

2.1.3. Scaled-up investigations.

Scaled-up investigations were conducted using the combined and the wash effluents as hydrolysis media. The wash effluent was selected in preference to the unhairing effluent based on the findings of the preceding optimisation experiments. The optimised hydrolysis conditions of the wash effluent (70°C, 6 hours) were utilised for both studies. The performance of the wash and combined effluents are compared in the following studies.

2.1.3.1. Solubilisation of the shavings during alkaline hydrolysis.

Figure 4.10 shows that slightly higher solubilisation was attained for the combined effluent, *viz.* 60.8% vs 53.7% solubilisation (wash effluent). Both samples were characterised by an initial pH of above 11 (pH 11.04 and 11.21, wash and combined effluents respectively).

Complete degradation of the shavings into fragments of the initial material occurred in both studies, neither sample showing any residual fibrous material in the dried solid residues. The dried residues were friable and disintegrated into coarse granules when crushed. Plate 4.5 shows the reduction in volume of the shavings hydrolysed in the wash effluent (initial dry weight of shavings 40g). The combined effluent solid residue was very similar in appearance.

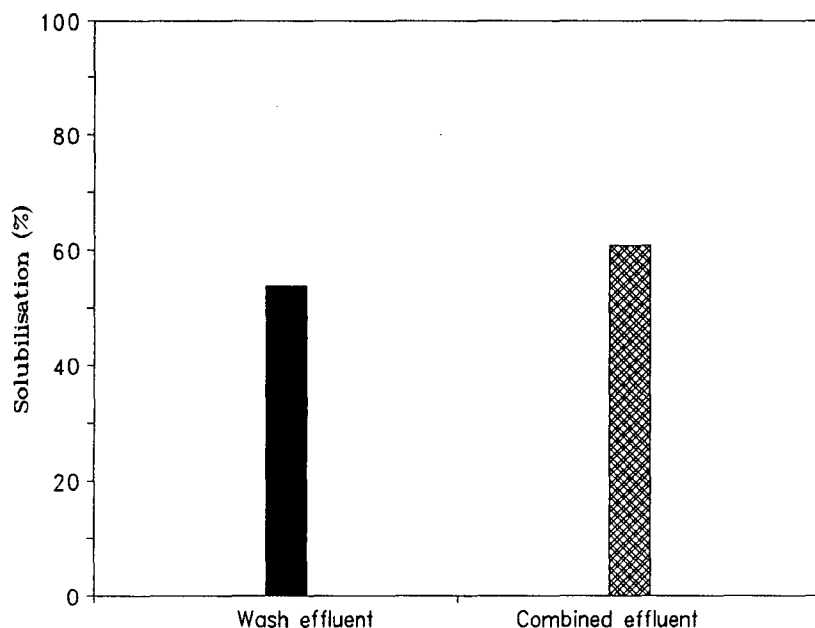


Figure 4.10. Solubilisation of the shavings in the scaled-up investigations using the wash and combined effluents.

2.1.3.2. Chromium content of the alkaline hydrolysis fractions.

Figure 4.11 compares the chromium concentrations of the hydrolysis filtrates (nett chromium solubilised) and the solid residues. Very small amounts of chromium were solubilised (0.14mg.L^{-1} wash effluent, 0.03mg.L^{-1} combined effluent), indicating that the chromium was apportioned to the solid residues as expected. The solid residues showed identical percentage chromium content (5.3%), but relative to the initial chromium content of the shavings (2.6 and 2.1%, wash and combined effluents respectively, Appendix II Table I), it is evident that the chromium was marginally better concentrated in the combined effluent solid residue (2.6 fold concentration) vs 2.2 fold for the wash effluent. The final pH of the sample filtrates ranged from 10.32 (wash effluent) to 10.57 (combined effluent).

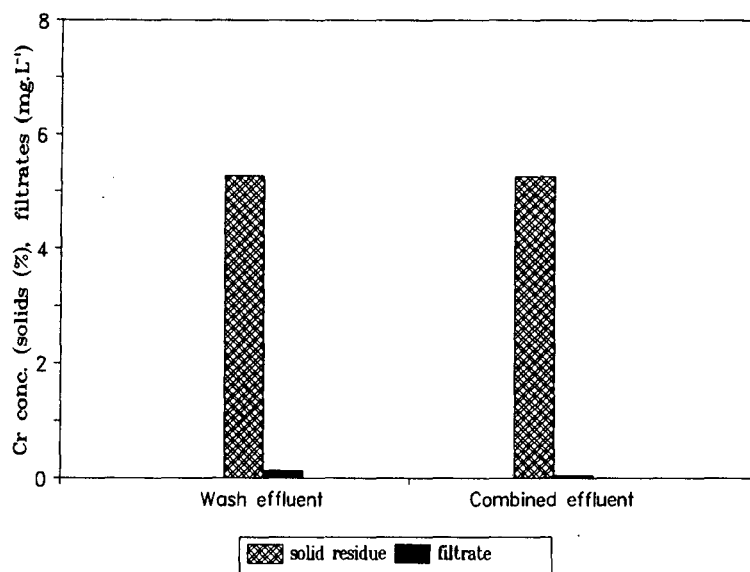


Figure 4.11. Chromium concentrations of the hydrolysis filtrates and solid residues from the scaled-up investigations using the wash and combined effluents.

2.1.3.3. Chromium recovery by acid wash.

As shown by Figure 4.12, chromium recovery was the same for either effluent, with 91% of the chromium recovered in each instance. In both investigations the acid washed solid residues were brown and the supernatants blue.

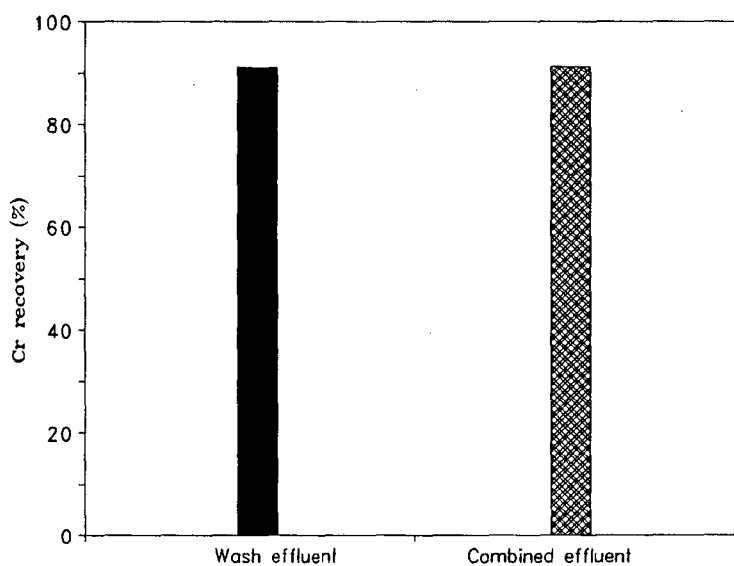


Figure 4.12. Chromium recovery for the scaled-up investigations using the wash and combined effluents.



Plate 4.5. Desiccated solid residues of the wet blue shavings hydrolysed in the wash effluent scaled-up investigation.

3. Discussion.

3.1. Alkaline effluents as substitute hydrolytic media.

This investigation demonstrated that the alkaline tannery effluents can be used as effective hydrolysis media for the solubilisation and detanning of wet blue shavings. The results were essentially similar to those of the lime-based investigation (Chapter 3), viz. solubilisation of the collagen and removal of the chromium as an insoluble precipitate.

The high alkalinity of the effluents, maintained throughout hydrolysis, promoted the formation of an insoluble chromium precipitate which once again settled well under gravity, leaving a surface clarified effluent and a compact sediment apparently appropriate for large scale industrial application. Re-solubilisation of the chromium from the precipitate during the acid wash recovery stage was also successfully accomplished. The chromium concentrations of the hydrolysis filtrates were, in most cases, well below the legal discharge limit of 0.5mg.L^{-1} (Rawlings *et al*, 1987), but in a few instances the chromium concentration approached, and even exceeded, the 0.5mg.L^{-1} threshold concentration (Figures 4.3, 4.4, 4.8 and 4.9). In addition, the high pH of the unhairing effluent was not automatically conducive to high protein solubilisation. This was shown to be related to the chemical nature of the effluent and will be discussed below.

3.2. The chemical characteristics of the effluents.

As shown in Table 4.1, all three effluents possessed the essential prerequisite of high alkalinity (due to the presence of hydroxide and sulphide) on which the success of this process depends. This obviated the need for supplementary lime addition. Analysis showed that the concentrations of the chemicals present in the wash effluent were less than those of the unhairing and combined effluents, although not as prominently so for the latter effluent. The very high sodium and chloride contents of the combined effluent suggest that the rinsing waters used to desalt the hides were incorrectly discharged together with the alkaline effluents in this instance, although the higher salinity did not appear to influence the process. Furthermore, no chromium should have been detected in any of the effluents, since all three were generated prior to the tanning stage. The presence of chromium in the effluents can only be ascribed to incorrect discharge procedures at the tannery, resulting in contamination of the alkaline effluents with residual chromium from the tanning liquors.

3.3. Optimisation of hydrolysis conditions.

The hydrolysis conditions could again be optimised for chromium recovery at the expense of solubilisation, or alternatively, to promote solubilisation as well. The latter required more drastic treatment conditions. Since use was made of the inherent alkalinity of the effluents, only the temperature and duration of hydrolysis required optimisation. Optimisation studies were only performed on the unhairing and wash effluents.

3.3.1. Hydrolysis temperature.

As occurred with the temperature investigations using fresh water and lime (Chapter 3), a progressive increase in solubilisation with temperature was noted for the wash effluent, particularly between 50 and 70°C (Figure 4.2), indicating the suitability of this effluent for solubilisation. The small increase in solubilisation afforded by increasing the hydrolysis temperature to 80°C was considered insignificant for the anticipated heating cost involved. Accordingly, 70°C was selected as the optimum temperature for solubilisation. Conversely, variation of the temperature of the unhairing effluent did not produce the expected increase in solubilisation (hydrolysis duration 12 hours), although the shavings were completely degraded in structure. This ability of the alkaline conditions to degrade the macrostructure of the shavings, but not solubilise the protein, is attributed to the high protein content of the crude unhairing effluent (ie. prior to hydrolysis, 5 591mg.L⁻¹ TKN, Table 4.1). It is postulated that this initially high protein content restricted the capacity of the effluent for further protein solubilisation during hydrolysis. The observed decrease in solubilisation recorded for the 80°C unhairing effluent sample may be due to precipitation of some of the solubilised protein. Since this decrease corresponded to the highest hydrolysis temperature, it is suggested that this may be due to the increased temperature endeavouring to enhance solubilisation, thereby resulting in the formation of a super-saturated protein solution, with subsequent protein precipitation.

Chromium recovery by acid wash was once again highly efficient and essentially independent of variation in the hydrolysis temperature (Figure 4.5). This is illustrated by the essentially complete recovery (100%) from the 50°C wash effluent cake, which had only solubilised to a very small extent (8.4%). Only marginally higher chromium recovery resulted from the wash effluent samples. Therefore, if detanning is the sole objective, lower temperatures can be employed using an effluent with a suitably high alkalinity and the chromium recovered at the expense of solubilisation. If the objective is to optimise both chromium recovery and solubilisation, it requires use of the wash effluent (ie. initial protein content conducive to protein solubilisation) and a hydrolysis temperature of at least 70°C.

The chromium levels in the filtrates warrant further discussion. As can be seen from the results for the wash effluent (Figure 4.4), relatively high chromium solubilisation occurred in the samples hydrolysed at 50 and 60°C, followed by a rapid decline in the chromium levels for the higher temperatures ($\geq 70^\circ\text{C}$). This indicates that chromium solubilisation is temperature dependent and a temperature of at least 70°C should be selected to avoid the generation of a residual hydrolysis filtrate with a chromium concentration above the legal discharge limit. This result, in contrast to the results obtained in Chapter 3, appears to support the earlier finding of Alves dos Reis and

Beleza (1991a), namely that the selection of a sufficiently high hydrolysis temperature is fundamental to the generation of a chromium-free hydrolysis filtrate. On the basis of the findings above, the established optimum temperature of the wash effluent (70°C) was used to evaluate the effect of a varying hydrolysis period on solubilisation and chromium recovery.

3.3.2. Hydrolysis period.

Solubilisation in the unhairing effluent appeared to be a function of time for the first 6 hours, as shown by the increase in solubilisation with longer hydrolysis periods (Figure 4.7). The 12 and 24 hour samples, in accordance with the results obtained for the temperature study above (Figure 4.2), indicated an apparent decrease in solubilisation. These findings indicate that the unhairing effluent initially has some capacity for solubilisation but, as was evident with temperature optimisation, longer hydrolysis durations may have enhanced solubilisation to a super-saturated state, resulting in precipitation of the protein beyond 6 hours. The wash effluent again showed a more constant profile of solubilisation with time, with an initial stage of rapid solubilisation again evident as shown by the approximately 60% of the total solubilisation that occurred within the first hour of hydrolysis. Since over 96% of the total solubilisation was recorded at 70°C within the first 6 hours of hydrolysis, longer durations are considered unnecessary, and 6 hours was therefore selected as the optimum period for solubilisation.

As with the temperature studies, the duration of hydrolysis also affected chromium solubilisation, this reflected by the higher concentrations of solubilised chromium in the 1 hour (unhairing effluent) and 1–2 hours (wash effluent) hydrolysis filtrates, and the rapid declines thereafter (Figures 4.8 and 4.9). Since the chromium concentrations represented nett chromium solubilisation, it would appear that higher concentrations of chromium did in fact solubilise during the early stages of hydrolysis and subsequently precipitated as hydrolysis progressed. What induced the initial increase in chromium solubilisation is unknown, but it is clear that a hydrolysis duration of at least 6 hours should be selected to avoid this. Furthermore, alkaline hydrolysis may also have the ability to scrub the effluent of solubilised chromium if performed for at least 6 hours at a temperature of 70°C or higher. This is of obvious relevance where the chromium concentration of the crude effluent used in hydrolysis is above the legal chromium discharge limits. Because the same effect was observed with both effluents, and in both instances for shorter hydrolysis periods, it is unlikely that this was due to experimental error. It is also important if the sole objective is chromium recovery, since to avoid generating an effluent containing chromium above the legal discharge limits, at least 6 hours of treatment at 70°C appears to be necessary. It would also have the additional advantage of higher protein solubilisation. Analysis of the wash effluent cakes from this study again showed only marginally

higher chromium recovery and high recovery for both effluents after only 1 hour of hydrolysis, suggesting that at 70°C, release of the chromium from the solid material is accomplished very rapidly (Figure 4.10). On the basis of these findings, the wash effluent was selected as the superior individual process effluent, with 70°C (hydrolysis temperature) and a hydrolysis period of 6 hours the optimal hydrolysis conditions. These observations were utilised in the scaled-up investigations.

3.4. Scaled-up investigation.

In view of the similar chemical characteristics of the wash and combined effluents, the optimum hydrolysis conditions of the wash effluent were adopted for use with the combined effluent. The scale-up investigations involved a proportionate ten-fold scale-up to maintain a 75:1 loading ratio (medium:shavings). The results for the wash effluent scaled-up investigation indicated no decrease in efficiency, with regard to either solubilisation or chromium recovery. The combined effluent gave very similar results to that of the wash effluent, indicating that either effluent can readily be substituted for lime and fresh water. The results for these scaled-up investigations clearly indicate that this process has potential for use on an even larger scale.

4. Conclusion.

1. Alkaline tannery effluents can be used as effective substitute hydrolysis media for lime and fresh water for the detanning of wet blue shavings.
2. Collagen protein is degraded and solubilised during hydrolysis, substantially reducing the volume of the solid waste.
3. Of the three alkaline effluents tested, all three were found to be effective for detanning wet blue shavings, but the high protein content of the unhairing effluent reduces its capacity for protein solubilisation. It does, however, still appear to degrade the macrostructure of the protein.
4. The wash effluent was established to be the better of the two single process effluents. The combined effluent was shown to be of similar efficiency to the wash effluent for detanning and protein solubilisation.
5. Hydrolysis conditions of 70°C (hydrolysis temperature) and 6 hours (hydrolysis period) are considered optimum for detanning and protein solubilisation. Shorter durations and lower operating temperatures are sufficient if detanning is the sole objective, this at the expense of protein solubilisation.
6. Ten-fold scale-up investigations using the wash and combined effluents respectively, did not decrease the efficiency of the treatment process with respect to either protein solubilisation or chromium recovery. The results suggest larger industrial scale-up application studies are warranted.

CHAPTER 5

INDUSTRIAL-SCALE INVESTIGATION

1. Introduction.

Once the exploratory investigations had established the potential of the alkaline effluents as substitute media for the treatment of wet blue shavings (Chapter 4), the next step was to establish whether this process could be scaled up to an industrial level. Industrial-scale investigations were undertaken on the premises of Exotan (Pty) Ltd, a commercial tannery processing approximately 1 500 hides per day and generating roughly 4 000kg of waste wet blue shavings per month (Bessinger 1993, Hobson, 1993). The combined effluent was the sole alkaline medium utilised in these investigations.

In the first investigation, wet blue shavings were investigated as the solid waste material and the optimum loading ratio of shavings to effluent was determined. Four loading studies (wet weight: 50, 100, 150 and 220kg) were undertaken and the effect of the loading ratio on solubilisation and chromium recovery was established. The decrease in physical size of the shavings during hydrolysis (size reduction) was also investigated. A hydrolysis period of six hours was selected for each loading study on the basis of the findings in Chapter 4. The second investigation explored whether this treatment process could be extended to include other chrome-tanned solid wastes, namely wet blue splits and finished leather trimmings. A heavy bovine hide may yield at least 0.2kg of trimmings and larger quantities of unmarketable split are frequently generated (Bessinger, 1993). Due to the larger size of the splits and trimmings relative to the shavings, the hydrolysis period was extended to 24 hours. The primary concern in the latter investigation was whether the solid material would solubilise and the effect, if any, of alkaline hydrolysis on chromium recovery.

2. Results.

A brief analysis of the crude effluent (pH and chromium concentration) utilised in each industrial-scale investigation was undertaken, and the results are shown in Table 5.1. This verified that the effluent was of a sufficiently high pH for use in hydrolysis and enabled comparison of the pre- and post-hydrolysis filtrate chromium concentrations.

Table 5.1. The pH and chromium concentration of the crude effluent used in each industrial-scale investigation.

	pH	chromium concentration (mg.L ⁻¹)
50kg loading study	11.41	1.37
100kg loading study	12.29	3.71
150kg loading study	11.58	2.58
220kg loading study	12.01	3.02
splits and trimmings	11.48	1.74

2.1. Solid waste material - wet blue shavings.

2.1.1. Solubilisation of the shavings during alkaline hydrolysis.

Figure 5.1 compares the solubilisation of the shavings for the 50–220kg loading studies. Because the increased quantity of shavings precluded desiccation prior to hydrolysis, the moisture content of the shavings, determined for each loading study, was accounted for in the solid residue dry weight determinations. While the 50 and 100kg loading studies were characterised by a constant pH during hydrolysis (Appendix II Table V), the 150 and 220kg loading studies, however, showed a progressive decrease in pH (Table 5.2) (pH analysis - universal pH indicator).

Table 5.2. The pH readings of the effluent media during hydrolysis for the 150 and 220kg loading studies.

Time (hours)	hydrolysis medium pH	
	150kg	220kg
0.08	11	10
0.25	11	9.5
0.50	9	9.5
0.75	9	9
1	8.5	8.5
2	8.5	8.5
3	8.5	8.5
4	8	8
5	8	8
6	8	7.5

In both loading studies the most marked decrease in pH with time occurred during the first hour of hydrolysis.

Table 5.3 outlines the loading ratio of medium:shavings for each loading study. Figure 5.1 shows that solubilisation is a direct function of the loading ratio, with the highest overall solubilisation occurring in the 50kg loading study, followed by decreased solubilisation thereafter with increasing starting weights of material. Approximately 30% solubilisation (46% of the maximum solubilisation obtained) occurred within the first 5 minutes of the 50kg study. During this stage the shavings were degraded into an unstructured mass of fibre. Maximal protein solubilisation occurred within 1 hour (57% solubilisation), with all the shavings completely degraded to a dark green, silt-like residue. A similar maximum solubilisation (58%) occurred in 6 hours in the 100kg loading study. Approximately 90% of this solubilisation occurred within the first 3 hours of hydrolysis (51% solubilisation). Examination of the 100kg desiccated solid residues indicated that fragments of the shavings still remained upon termination of hydrolysis. Significantly reduced solubilisation occurred for the 150 and 220kg loading studies, with 6 hour solubilisation values of 42 and 30% respectively. The majority of these solid residues comprised shavings showing some degree of degradation (reduced in size), but with a few essentially undigested shavings still evident. Plates 5.1 and 5.2 illustrate the desiccated solid residues of the 50 and 220kg loading studies. Solubilisation intermediate of the two occurred in the 100 and 150kg analyses.

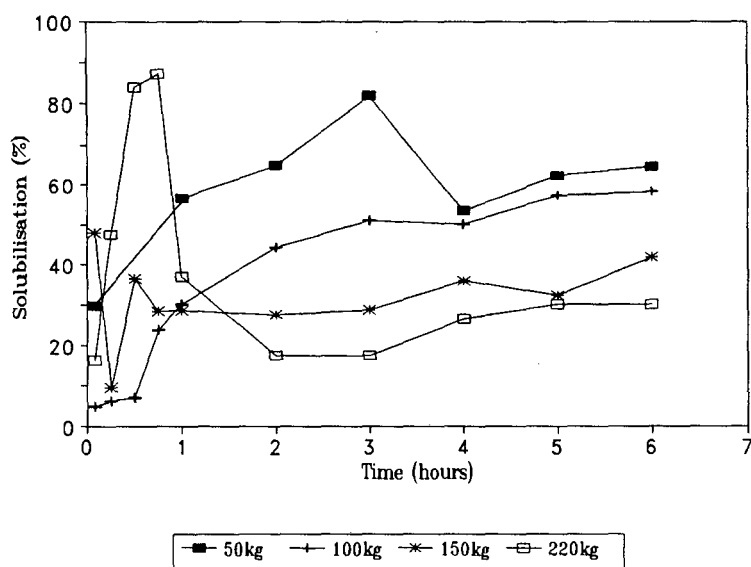


Figure 5.1. Solubilisation profiles for the 50–220kg loading studies.



Plate 5.1. Alkaline hydrolysis filtrates and desiccated solid residues of the 50kg loading study.

The compaction of the solid residue material that occurred during drying does not give a clear indication of the complete degradation observed, particularly for the 1–6 hour samples where only a silt-like residue remained after hydrolysis. The 5 minute solid residue (wet) consisted of a unstructured, spongy mass of fibrous material.

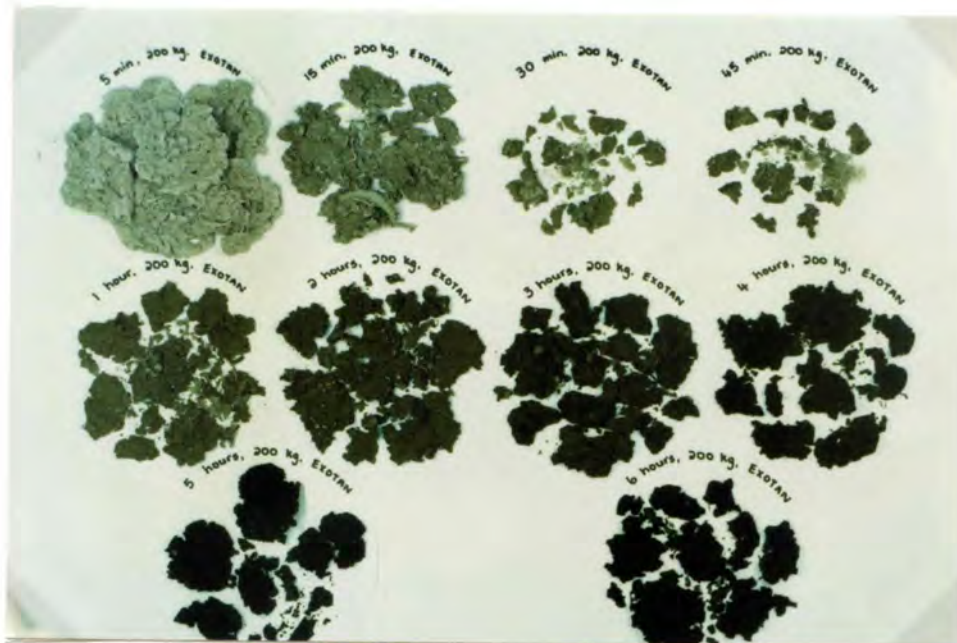


Plate 5.2. Desiccated solid residues of the 220kg loading study.

The 5 minute solid residue was blue-grey in colour, the residues of subsequent samples a progressively darker green-brown colour. The dark colour of these latter samples masked the semi-intact shavings still present in the solid residues.

Table 5.3. Loading ratio of medium to shavings for each industrial-scale loading study.

	loading ratio of medium:shavings (L:kg)
50kg loading study	49:1
100kg loading study	24:1
150kg loading study	16:1
220kg loading study	11:1

2.1.2. Size reduction of the shavings during alkaline hydrolysis.

Figure 5.2 compares the reduction in physical size of the shavings during hydrolysis for the 100–220kg loading studies. No size reduction investigation was undertaken for the 50kg loading study, but on the basis of the degradation observed during hydrolysis (Figure 5.1 and Plate 5.1), it is clear that the entire solid residue would have passed through a 4mm² sieve for the 1 hour and subsequent samples. In the 100kg analysis, 88% of the solid residue was ≤4mm² after only 2 hours of hydrolysis. This increased to 92% after 6 hours. Approximately 60% of the 150 and 220kg solid residues were ≤4mm² after 6 hours of hydrolysis. Plates 5.3 and 5.4 show the relative quantities of material retained in the sieve at each sampling time for the 100 and 220kg analyses respectively. Included for comparison are the quantities of shavings (dry weight) calculated to have been present in an equivalent 5L sample volume at the start of the experiment. The 150kg analysis showed very similar results to the 220kg analysis.

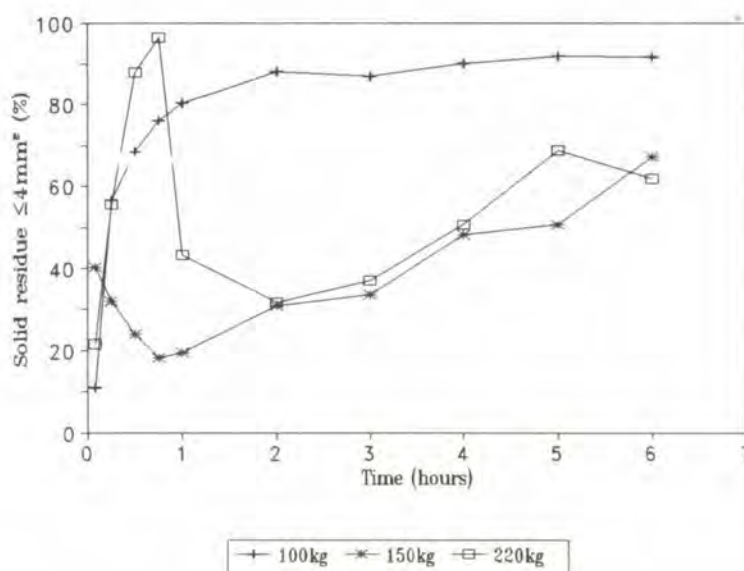


Figure 5.2. Size reduction profiles of the 100–220kg loading studies.



Plate 5.3a. Desiccated solid residues (5 minutes–1 hour) retained during size reduction analysis of the 100kg loading study.



Plate 5.3b. Desiccated solid residues (2–6 hours) retained during size reduction analysis of the 100kg loading study.



Plate 5.4a. Desiccated solid residues (5 minutes–1 hour) retained during size reduction analysis of the 220kg loading study.

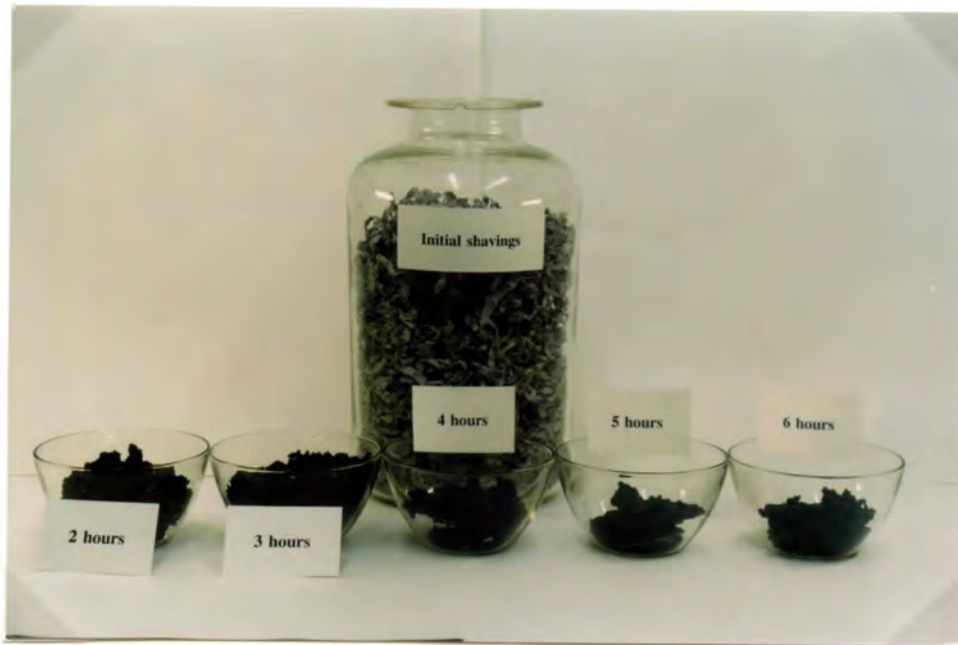


Plate 5.4b. Desiccated solid residues (2–6 hours) retained during size reduction analysis of the 220kg loading study.

2.1.3. Chromium content of the alkaline hydrolysis fractions.

Figures 5.3–5.6 show the chromium concentrations of the hydrolysis filtrates and solid residues for the 50–220kg loading studies, the concentrations of the filtrates representing total chromium solubilised. The low filtrate concentrations show that the bulk of the chromium remained associated with the solid residues, and subsequently concentrated during solubilisation. The instances of filtrate chromium concentration exceeding 0.5mg.L^{-1} [see Figures 5.5 (150kg) and 5.6 (220kg)] will be discussed below.

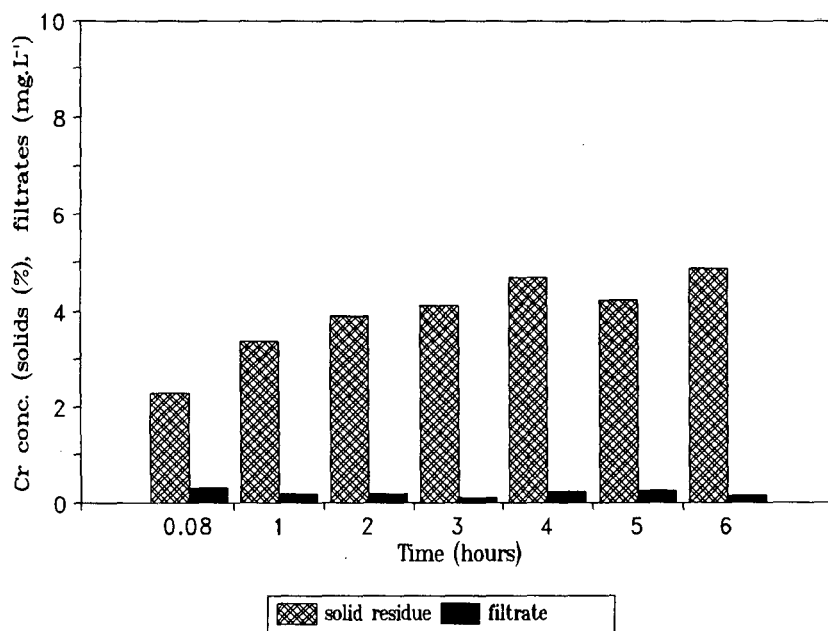


Figure 5.3. Chromium concentrations of the hydrolysis filtrates and solid residues of the 50kg loading study.

The 50kg study filtrates contained $0.11\text{--}0.25\text{mg.L}^{-1}$ chromium. The chromium was concentrated 1.5–3.2 fold in the solid residues (1.5% initial chromium content, Appendix II Table I).

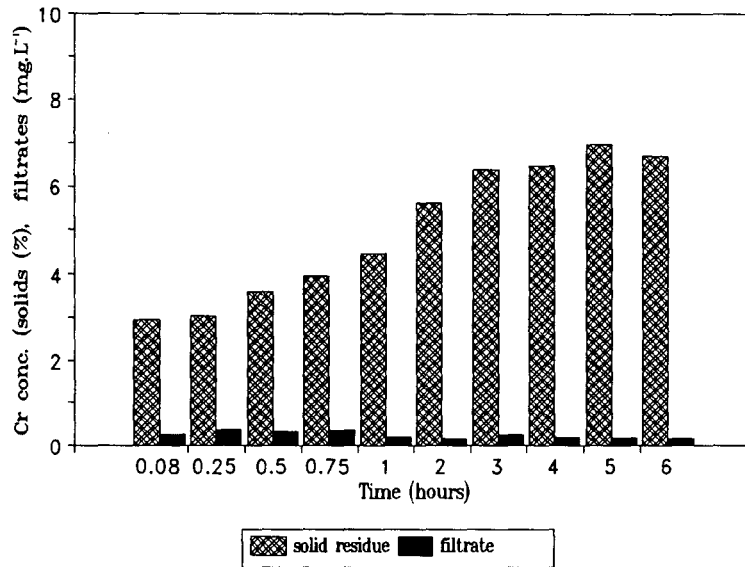


Figure 5.4. Chromium concentrations of the hydrolysis filtrates and solid residues of the 100kg loading study.

The 100kg study filtrates contained 0.15–0.37mg.L⁻¹ chromium. The chromium was concentrated 1.0–2.4 fold in the solid residues (3.0% initial chromium content, Appendix II Table I).

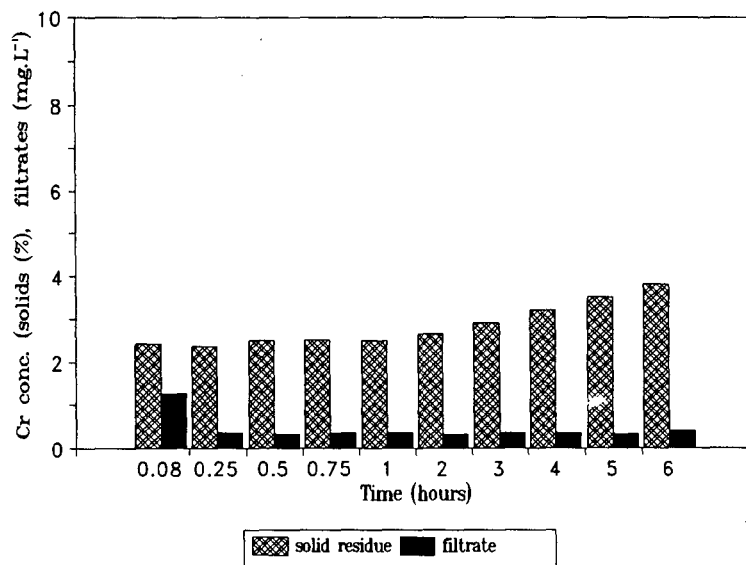


Figure 5.5. Chromium concentrations of the hydrolysis filtrates and solid residues of the 150kg loading study.

The 150kg study filtrates contained 0.31–1.26mg.L⁻¹ chromium. The chromium was concentrated 1.1–1.8 fold in the solid residues (2.1% initial chromium content, Appendix II Table I). Note the very high chromium concentration of the 5 minute sample (1.26mg.L⁻¹), followed by significantly reduced chromium concentrations for all subsequent samples (≤ 0.41 mg.L⁻¹).

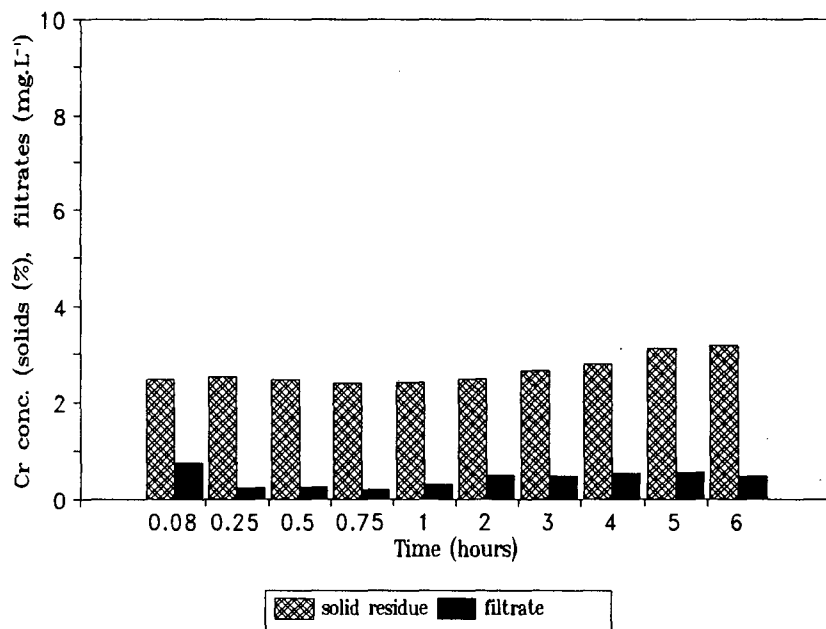


Figure 5.6. Chromium concentrations of the hydrolysis filtrates and solid residues of the 220kg loading study.

The 220kg study filtrates contained 0.20–0.73mg.L⁻¹ chromium. The high chromium concentration of the 5 minute sample (0.73mg.L⁻¹) decreased to ≤ 0.25 mg.L⁻¹ between 15 and 45 minutes. Thereafter, the concentration of solubilised chromium increased again (up to 0.55mg.L⁻¹). The chromium was concentrated between 1.1 and 1.5 fold in the solid residues (2.1% initial chromium content, Appendix II Table I).

2.1.4. Chromium recovery by acid wash.

Figure 5.7 compares the chromium recoveries of the 50–220kg loading studies. Between 88 and 100% of the chromium was recovered from all samples of the 50, 100 and 220kg analyses. Lower chromium recovery occurred for the 150kg loading study, with between 68 and 83% recovery. All loading studies showed high recovery after only 5 minutes of hydrolysis (> 83%). Plate 5.5 shows the acid wash supernatants and solid residues of the 50kg loading study, with the 100–220kg samples essentially similar in appearance. The supernatants were all blue in colour and the solid residues all brown to black, the latter again masking any bleached appearance of the acid washed solid residues.

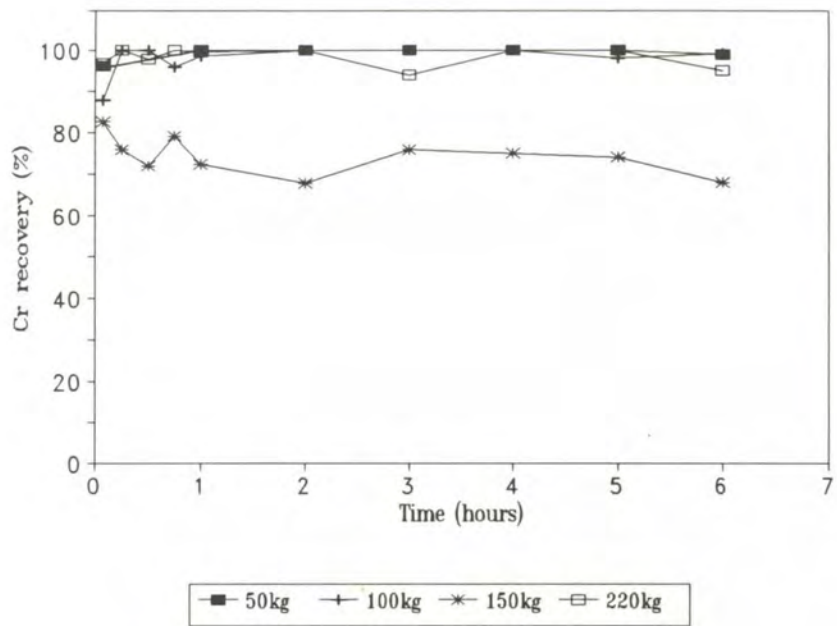


Figure 5.7. Chromium recovery profiles of the 50–220kg loading studies.



Plate 5.5. Acid wash supernatants and solid residues of the 50kg loading study.

2.1.5. Chemical profile of the post-hydrolysis effluent medium.

The post-hydrolysis effluent was analysed in order to establish and assess changes which could affect subsequent discharge or treatment procedures. The chemical profile for the 100kg loading study is shown in Table 5.4.

Table 5.4. Chemical profile of the final effluent discharged after the 100kg loading study.

pH	9.73
conductivity (mS.m ⁻¹)	3 385
alkalinity - phenolphthalein (mg.L ⁻¹) - methyl orange (mg.L ⁻¹)	250 1 659
PV (mg.L ⁻¹)	1 562
COD (mg.L ⁻¹)	15 752
ammonia (mg.L ⁻¹)	313
nitrate (mg.L ⁻¹)	350
TKN (mg.L ⁻¹)	2 903
sodium (mg.L ⁻¹)	6 900
calcium (mg.L ⁻¹)	420
sulphate (mg.L ⁻¹)	2 158
sulphide (mg.L ⁻¹)	125
chloride (mg.L ⁻¹)	13 883
chromium (mg.L ⁻¹)	0.29
fat, oil or grease (mg.L ⁻¹)	64

Both the pH and the chromium concentration of the final effluent were reduced relative to the levels in the initial effluent utilised in hydrolysis. Chromium, in particular, was reduced 92% relative to the initial effluent (refer to Table 5.1). The settling rate of the heated final effluent (laboratory settling) is shown in Figure 5.8. The bulk of visible settling was completed within 3–5 minutes (0–30 minutes not shown). Thereafter, the precipitated sediment continued to compact, as shown by the gradual increase in the volume of clarified effluent with time. Obviously a proportionately longer period was required for settling of the larger reaction volume in the industrial-scale investigations. As will be discussed below, these settling rates were retarded by convection currents which continued for a short period after agitation was removed. A settling period of 3–4 hours generally proved sufficient to produce a well clarified surface effluent.

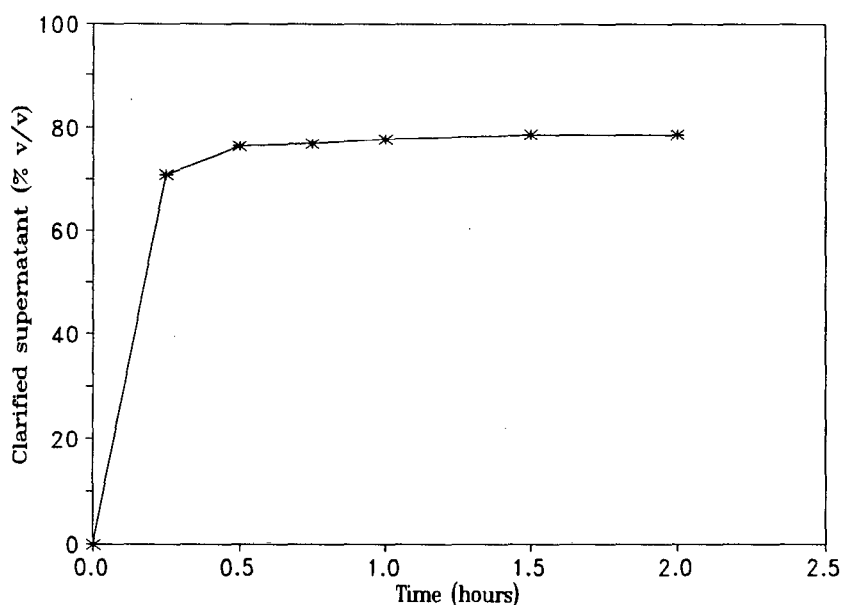


Figure 5.8. Settling rate of the heated final effluent (representative sample of the 100kg loading study).

2.2. Solid waste material - wet blue splits and finished leather trimmings.

The application of this treatment process to the alternative tannery solid wastes *viz.* wet blue splits and finished leather trimmings was also investigated. Small quantities of splits and trimmings were combined in a single hydrolysis procedure and a similar programme to that used for the shavings was followed.

2.2.1. Solubilisation of the splits and trimmings during alkaline hydrolysis.

The pH remained constant throughout hydrolysis (Appendix II Table V). The pH and chromium concentration of the initial effluent is shown in Table 5.1. Inability to positively identify (by marking) the individual pieces of solid waste, precluded an accurate evaluation of solubilisation. Instead, a subjective assessment based on visual observations was made.

These observations indicated that:

- 1). The thinner sheep leather trimmings degraded rapidly compared to the thicker wet blue splits and bovine trimmings.
- 2). The sheep trimmings were completely fragmented by 5 hours (fragments $\pm \leq 1\text{cm}^2$). The wet blue splits required at least 3 hours before smaller pieces of material started to

dissociate from the parent portions. The splits never completely fragmented. The bovine leather trimmings were even more resistant to solubilisation and the rate of degradation even slower than for the wet blue splits. Samples of particularly thick bovine trimming were essentially undegraded after even 24 hours of hydrolysis.

- 3). One of the first indications of solubilisation involved the development of a gelatinous (rubbery) texture to the solid material. Longer hydrolysis periods resulted in cracking of the surface layer and subsequent sloughing off of the material to expose the now gelatinous interior. The outer edges of the sheep trimmings became gelatinous and rendible after only 30 minutes of hydrolysis. Cracking of the grain layer was evident by 1 hour. The wet blue splits became gelatinous (edges) after approximately 45 minutes. Cracking of the grain layer was evident by 5 hours. Surface cracking of the thinner bovine trimmings was evident by 6 hours.
- 4). The light blue-grey colour of the splits (onset of hydrolysis) darkened to a green colour (15 minutes). When viewed in cross-section, this was evident as a thin green layer on each outer margin of the split. These layers slowly increased in diameter as hydrolysis progressed. The same feature was evident in the bovine trimmings, but was not as distinct due to the dye present in the trimmings.
- 5). A significant quantity of fine (silt-like) green precipitate was evident on the base of the bin following discharge of the bin contents. This precipitate resembled that previously observed with hydrolysis of the shavings.

2.2.2. Chromium content of the alkaline hydrolysis fractions.

Figure 5.9 shows the chromium concentrations of the hydrolysis filtrates and solid residues for the splits and trimmings, the chromium content of the hydrolysis filtrates representing total chromium solubilised. The filtrates contained very low concentrations of chromium, between 0.15 and 0.39mgL⁻¹. The solid residues contained between 2.9 and 4.2% chromium (splits) and 2.2–5.4% chromium (trimmings). This represented a 1.0–1.4 fold and a 1.1–2.7 fold concentration of the chromium respectively (initial chromium content 3.0% (splits) and 2.0% (trimmings), Appendix II Table I).

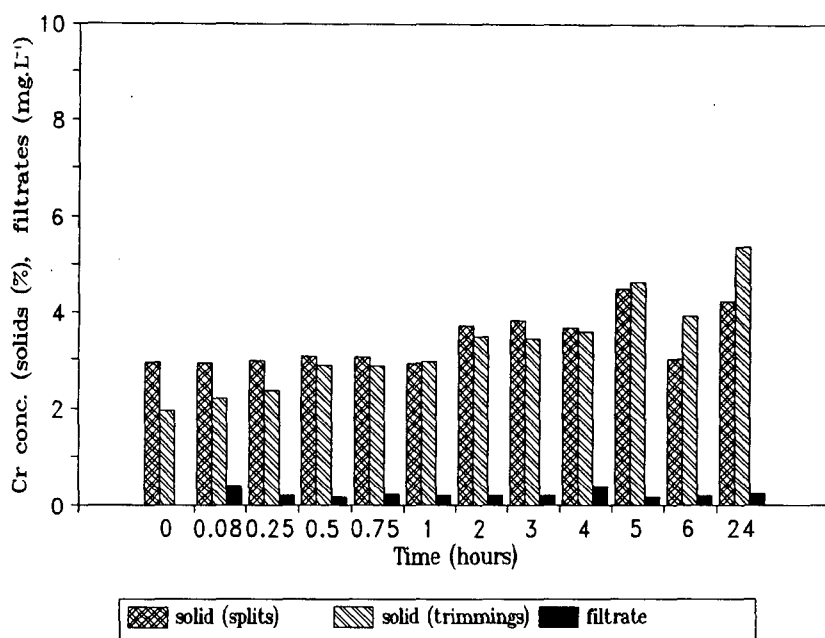


Figure 5.9. Chromium concentrations of the hydrolysis filtrates and solid residues for the splits and trimmings.

2.2.3. Chromium recovery by acid wash.

As shown in Figure 5.10, marginally higher levels of chromium were recovered from the wet blue splits (34–100% recovery) compared to between 10 and 92% recovery from the trimmings. The zero hour values show the chromium recovered without the benefit of preceding hydrolysis (splits 34% vs trimmings 10%). Only 5 minutes of hydrolysis increased chromium recovery from the splits 2.2 fold (75% recovery). This increased to nearly 3 fold after 6 hours (99% recovery). Chromium recovery from the trimmings increased 3.5 fold after only 5 minutes (36% recovery) and 8.9 fold after 6 hours (91% recovery). The 24 hour samples of both splits and trimmings showed 100% recovery. The acid wash supernatants for the wet blue splits were blue and the solid residues brown to black. The dye present in the finished leather trimmings coloured the acid wash supernatants, thereby masking the blue colour characteristic of solubilised chromium. This is shown in Plate 5.6. The acid washed solid residues of the trimmings were primarily dark-brown to black.

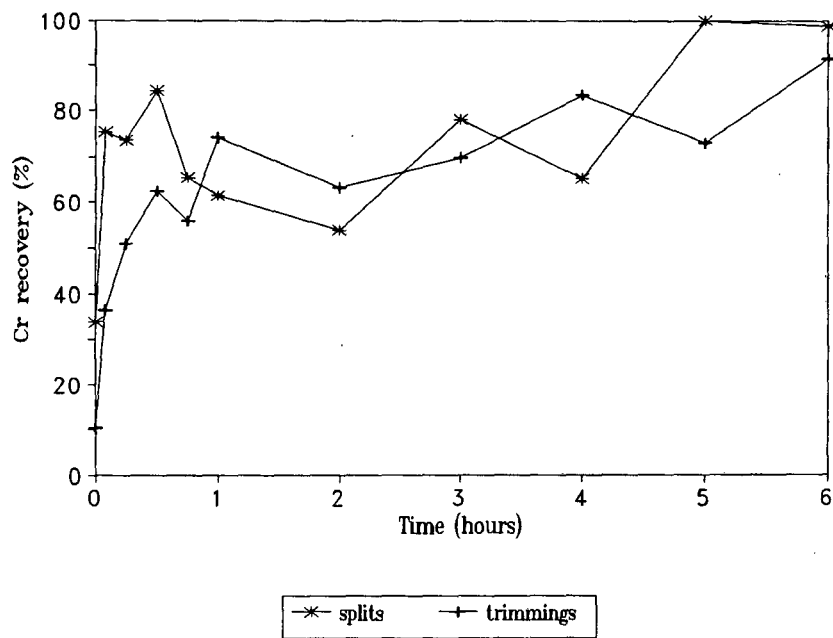


Figure 5.10. Chromium recovery profiles for the splits and trimmings.



Plate 5.6a. Acid wash supernatants and solid residues (0 minutes–1 hour) of the finished leather trimmings.



Plate 5.6b. Acid wash supernatants and solid residues (2–6 hours) of the finished leather trimmings.

3. Discussion.

3.1. An industrial-scale alkaline hydrolysis treatment process.

The results obtained in this study appear to confirm the potential of the effluent-based alkaline hydrolysis process for the treatment of solid chrome wastes on an industrial scale, and its potential applicability to shavings, wet blue splits and finished leather trimmings is demonstrated. An exploratory six hour hydrolysis period was selected on the basis of the findings in Chapter 4, this also being conducive to industrial-scale application in that it allows completion of a treatment process in a single working day. The hydrolysis temperature was increased to approximately boiling point to facilitate agitation of the increased mass of material (steam provides both heat and agitation), and possibly to facilitate protein solubilisation, although the earlier investigations (Chapters 3 and 4) showed minimal improvement in solubilisation with an increase in the hydrolysis temperature above 70°C (Figures 3.4 and 4.7). A relatively long post-hydrolysis settling time (ca. 3 hours) was required to produce a suitably clarified effluent for discharge, as the turbulence created by heat and agitation during hydrolysis continued for a period after agitation was ceased, retarding settling temporarily.

The effluent used in each investigation was highly alkaline, with a pH ranging between 11.41 and 12.29 (Table 5.1). Minor pH variations in the initial effluent may be attributed to varying degrees of sulphide oxidation, induced by forced aeration of the effluent in the sulphide oxidation tank prior to collection for hydrolysis. The very high chromium concentrations of the initial effluents (1.37–3.71mg.L⁻¹, Table 5.1) once again indicated considerable contamination with tanning liquors but, as previously mentioned in Chapter 4, this did not have any apparent negative effect on the hydrolysis process.

3.2.1. Effect of loading ratio on solubilisation and size reduction.

A notable pH decline was observed for the 150 and 220kg analyses. This tendency is attributed to the detanning reaction and to neutralisation of the pH by acid released from the shavings during hydrolysis (Taylor *et al*, 1990). Whilst this effect may be beneficial in that it produces a final effluent of low alkalinity, a declining pH will obviously also reduce the ability of the effluent to solubilise protein. This is borne out by the significantly reduced solubilisation recorded for the 150 and 220kg batches (Figure 5.1). Discharge of a highly alkaline final effluent is not necessarily problematic when an on-site effluent treatment plant is available. Where this is not the case, the relative advantages of effective solubilisation (i.e. lower loading ratios), or of lower final pH (i.e. higher loading ratios) must be compared and an acceptable loading ratio selected in accordance.

The anomalous peaks and troughs observed for the solubilisation profiles in Figure 5.1 are due to non-homogeneous mixing of the bin contents. This was particularly evident at the onset of hydrolysis for the 150 and 220kg loading studies where the increased mass of material rendered initial agitation difficult. The material either settled, leaving a sparse surface layer which resulted in less material collected per unit volume in the sample aliquot (perceived as an apparently "high" solubilisation i.e. peaks), or the shavings accumulated near the surface and were not dispersed throughout the bin, resulting in the observed "troughs" (i.e. more material collected per unit volume).

The excellent solubilisation profiles of the 50 and 100kg loading studies (Figure 5.1) indicate a loading ratio very conducive to solubilisation (49:1 and 24:1 (effluent:shavings) respectively). If the peaks and troughs are ignored, it becomes evident that very little additional solubilisation occurred after 1 hour (50kg) or 2 hours (100kg). The significantly lower solubilisation recorded for the 150kg (16:1 loading ratio) and 220kg studies (11:1 loading ratio), the lack of a rapid initial solubilisation stage, and the declining solubilisation profiles across the full 6 hours of hydrolysis indicate that the maximum loading ratio for acceptable solubilisation lies between that of the 100 and 150kg studies (i.e. a loading ratio of *ca.* 20:1 (effluent:shavings)). Larger loads (i.e. higher loading ratios) would result in diminished solubilisation due to protein saturation and pH neutralisation of the effluent, whilst smaller loads, although solubilising to a greater extent, would leave the residual alkalinity of the effluent underexploited.

Size reduction was difficult to determine accurately because it was based on the ability of the degraded shavings to pass through a sieve (aperture 4mm²). Aliquots for size reduction analysis were collected at the same time as the solubilisation samples, resulting in similar peaks and troughs (Figures 5.1 and 5.2). In addition, clogging of the sieve apertures by larger shavings hampered the passage of smaller fragments, resulting in erroneously low values for size reduction. In spite of these experimental limitations, a general assessment of size reduction was possible. The determination of size reduction of the shavings is of relevance, since screening of the bin contents upon termination of hydrolysis to separate the solid residue from the supernatant is a possible option to settling of the bin contents, although this could also be performed on the settled solid residue. In this regard, an indication of the size of the fragments and the quantity of material able to pass through a particular sieve aperture must be known if effective separation is to be achieved. Such knowledge is also of significance for tanneries where the solid waste produced from such a treatment process must be removed for chromium recovery, should chromium recovery facilities not be available on the premises.

In agreement with the solubilisation results, size reduction of the 100kg samples was extensive, with only 8% of the shavings large enough to be retained by the sieve after 6 hours (Figure 5.2). Far less size reduction occurred for the 150 and 220kg loads over the 6 hour period (approximately 40% retention for both). This is again attributed to the strong neutralisation effect observed for these runs, and not to protein saturation since gradual, but continuous, size reduction was observed over the full 6 hour period. Plates 5.3 and 5.4 highlight the considerable decrease in volume of the solid residues relative to the initial quantities of shavings added (100 and 220kg studies).

3.2.2. Effect of loading ratio on chromium concentration.

The hydrolysis filtrates of the 50 and 100kg loading studies all contained chromium concentrations below the legal discharge limit of $0.5\text{mg}\cdot\text{L}^{-1}$ (Rawlings *et al*, 1987), even after 5 minutes of hydrolysis (Figures 5.3 and 5.4). The high pH maintained throughout hydrolysis favoured chromium precipitation as the hydroxide rather than chromium solubilisation. The hydrolysis filtrates of the 150 and 220kg batches, on the other hand, initially contained concentrations of chromium in excess of $0.5\text{mg}\cdot\text{L}^{-1}$ (see 5 min samples in Figures 5.5 and 5.6). These initially high concentrations of solubilised chromium rapidly dropped to below $0.5\text{mg}\cdot\text{L}^{-1}$ as hydrolysis progressed. However, unlike the 150kg study, after the initial decrease in the concentration of solubilised chromium, the 220kg loading study did show a gradual increase in solubilised chromium towards the end of hydrolysis (Figure 5.6). These initially high chromium concentrations in the 150 and 220kg studies, immediately subsequent to commencing hydrolysis, reflect the chromium contamination present in the effluent (refer to Table 5.1). What is of great significance is that this solubilised chromium was reduced to within the legal discharge limits within 5 minutes in the 50 and 100kg runs, and within 15 minutes for the larger loading studies. Therefore, as shown in the preliminary investigations in Chapter 4, the alkaline conditions appear to "scrub" the effluent of chromium, causing it to precipitate with the solid residue. The gradual increase in the chromium concentrations observed in the 220kg study filtrates correlate with the observed decrease in pH over 6 hours, which presumably causes some of the chromium to start resolubilising. This finding once again underlines the importance of an appropriate initial loading ratio, not only to optimise solubilisation, but also to ensure a post-hydrolysis filtrate which contains acceptable levels of chromium.

3.2.3. Effect of loading ratio on chromium recovery.

Chromium recovery from the solid residues was not affected by the loading ratio of shavings to effluent. The 50, 100 and 220kg residues all gave equally high chromium recovery (essentially 100%) following acid wash (Figure 5.7). The 150kg study surprisingly showed reduced

chromium recovery and, since no legitimate reason can be suggested for this unexpected result, it must therefore be attributed to experimental error. What is clear is that high chromium recovery was achieved whether the shavings were degraded or not. The practical implication of this is that a larger quantity of shavings can be added, at the expense of protein solubilisation, if chromium recovery is the sole objective. Indeed essentially complete chromium recovery was attained after only 5 minutes of hydrolysis. It would, however, be beneficial to hydrolyse for a longer period to effect size reduction, since drying of the residue after hydrolysis would be more rapid and a smaller quantity of acid would be required for leaching. One drawback of using a loading ratio significantly below the maximum capacity (e.g. the 50kg study), is that the shavings are so rapidly and so comprehensively degraded that the fine silt-like product takes longer to settle. Owing to the importance of size reduction, a loading ratio of *ca.* 20:1 (effluent:shavings) again appears to be optimal for both processes. Based on the overall solubilisation and size reduction results obtained, it is suggested that hydrolysis be terminated after 2 hours. This will allow approximately 45% solubilisation, but over 88% of the residue will be degraded to $\leq 4\text{mm}^2$, significantly reducing the volume of the waste (refer to Figures 5.1 and 5.2). Acid leaching of this residue should recover 100% of the chromium (Figure 5.7). The high pH of the post-hydrolysis effluent is the only drawback, but it could be combined with other less alkaline tannery effluents for subsequent treatment.

3.3. Chemical analysis of the final effluent (after hydrolysis).

The final effluent of the 100kg loading study was selected for analysis since it was closest to the suggested optimum loading ratio for both solubilisation and chromium recovery proposed above. Chemical analyses were conducted on the effluent upon termination of hydrolysis (i.e. > 6 hours) and the findings are compared with the general chemical profile already established for the pre-hydrolysis effluent (Table 4.1).

In addition to the beneficial changes in pH and chromium concentration discussed above, extensive conversion of sulphide to sulphate was also noted. The initial effluent sulphide concentration was generally 3–4 times higher than the sulphate concentration (Table 4.1), whereas the final effluent showed extensive oxidation of sulphide to sulphate (sulphate 17 times higher than sulphide, Table 5.4). The deleterious effects of sulphide will be outlined in Chapter 6. The COD of the final effluent was higher than that of the initial effluent, both values far in excess of the proposed general discharge limits (Rawlings *et al*, 1987). Secondary treatment of the final effluent to deal with this aspect therefore remains a necessity. The TKN and nitrate concentrations of the final effluent were also higher after hydrolysis. This is clearly a consequence of protein degradation and solubilisation. General standard limits are not always specified for nitrate concentrations,

however, the ammonia concentration of the final effluent was more than thirty times the general standard limits (Rawlings *et al*, 1987). Conductivity, initially far in excess of the general standard limit (Rawlings *et al*, 1987), was only marginally decreased during hydrolysis. This is principally a function of dissolved salts in the effluent and therefore hydrolysis cannot be expected to cause a significant decrease in this reading.

3.4.1. Solubilisation of the splits and trimmings.

Despite the subjective procedure used for assessing solubilisation of the splits and trimmings, the results clearly showed that thicker splits and finished leathers were less susceptible to degradation and solubilisation, even under the extreme conditions employed. The observed poor solubilisation cannot be ascribed to an unfavourable loading ratio (combined loading ratio ~425:1 (effluent:solid wastes)), nor to a pH effect, as the small quantity of wet blue splits and finished leather trimmings did not induce any pH decrease in the hydrolysis medium (Appendix II Table VI). Therefore, the poor solubilisation must be related to the physical structure of the waste. In agreement with this, the thinner, softer and more elastic sheep trimmings appeared to be the most rapidly degraded. A hydrolysis period of 5 hours was sufficient to degrade this material to fragments. The bovine splits and trimmings were more resistant to solubilisation, the thicker cross-section and smaller surface area of this material obviously contributing to the observed poor solubilisation. Shredding the material, particularly the bovine splits and trimmings, to increase the surface area is a logical recommendation. This would presumably speed up the solubilisation process and bring it in line with results observed for the shavings. The layer of green-grey precipitate lining the base of the bin upon termination of hydrolysis was identical to that observed after hydrolysis with the shavings and is therefore assumed to be precipitated chromium hydroxide from the solubilised material.

3.4.2. Chromium concentrations of the hydrolysis fractions of the splits and trimmings.

The low chromium concentrations recorded for the hydrolysis filtrates (Figure 5.9), indicate that the chromium contained in the splits and trimmings once again did not solubilise during hydrolysis. This may be related to the small quantities of solid material added but, given the consistently low levels of chromium in the hydrolysis filtrates obtained for the more soluble shavings' investigations (Figures 5.3–5.6), larger quantities of shredded splits and trimmings would in all probability still produce a filtrate low in solubilised chromium. The heated alkaline conditions were again responsible for precipitating much of the chromium present in the effluent at onset of alkaline hydrolysis (refer to Table 5.1 and Figure 5.9 respectively).

The chromium concentrations of the solid wastes warrant further discussion. Since in the case of the splits and trimmings, individual pieces of material were collected for analysis at each sampling time, these concentrations should only reflect the chromium still associated with the collected solid sample and not include any precipitated chromium. Nevertheless, the splits and trimmings still showed a small, but significant, increase in chromium concentration as solubilisation slowly progressed (Figure 5.9). This suggests that some of the chromium released from the solid wastes must have remained associated with the solid residues, either from physical contact with the precipitated residue or, possibly, by electrostatic attraction. The slight variation in the chromium concentrations can also partly be ascribed to variation in the initial chromium content of the assorted pieces.

3.4.3. Chromium recovery from the hydrolysed wet blue splits and finished leather trimmings.

These findings show that slightly better chromium recovery was obtained from the splits, particularly during the early stages of alkaline hydrolysis (Figure 5.10). This may be ascribed to the fact that the trimmings had been subjected to a second tanning process (retan) resulting in more extensive cross-linkage. There is also likely to be far less unbound chromium (residual chromium) associated with these pieces than the splits, the latter most probably explaining the higher chromium recovery from the splits sampled immediately subsequent to commencement of, and during the early stages of, hydrolysis. After one hour of hydrolysis the levels of chromium recovered from the trimmings approached those of the splits, suggesting that precipitation of this residual chromium had occurred during alkaline hydrolysis.

The progressive improvement in chromium recovery from the splits and trimmings, observed with an increase in the hydrolysis period, suggests that the protein-chromium bonds were not all broken in the early stages of alkaline hydrolysis as occurred with the shavings, the latter enabling virtually complete recovery of the chromium after only 5 minutes of hydrolysis (Figure 5.7). Therefore, the hydrolysis period is of crucial importance to chromium recovery from the larger splits and trimmings. Based on the chromium recovery results for the shavings, it is likely that size reduction of the splits and trimmings (ie. shredding of the material to a size approximating that of the shavings) could improve the rate of detanning and possibly bring it in line with the results observed for the shavings. While further study is required to fully validate these suppositions, it is clear that the alkaline hydrolysis process can be used to treat, and to recover chromium from, the splits and trimmings. Size reduction of the solid wastes may well obviate the need for a longer hydrolysis period for both solubilisation and chromium recovery purposes.

4. **Conclusion.**

1. This process shows great potential for treating the large quantities of chrome-bearing solid waste produced by commercial tanneries. This is particularly true for wet blue shavings.
2. Increasing the loading ratio of shavings to effluent decreases the efficiency of protein solubilisation but has little or no effect on chromium recovery.
3. Virtually total recovery of the chromium was possible after only 5 minutes of hydrolysis for the 220kg loading study, however, a short hydrolysis period foregoes the benefits of size reduction and protein solubilisation.
4. A loading ratio of approximately 20:1 (effluent:shavings) is a suggested optimum for both solubilisation and chromium recovery.
5. The final effluent produced during hydrolysis still requires treatment, but the pH, chromium and sulphide levels are beneficially reduced during alkaline hydrolysis.
6. The splits and trimmings were not as extensively degraded during alkaline hydrolysis, but the treatment process did permit improved chromium recovery.
7. Shredding of the splits and trimmings is suggested in order to reduce the need for the longer hydrolysis periods shown to be necessary for protein solubilisation and chromium recovery.

CHAPTER 6

GENERAL DISCUSSION

6.1. Effluent-based alkaline hydrolysis as a treatment process.

The foregoing investigations show that hydrolysis of wet blue shavings (and to a lesser extent wet blue splits and finished leather trimmings) in alkaline tannery effluents, followed by a simple acid leaching step, permits separation of the chromium from the hide protein and recovery of this chromium in a potentially reusable form. This process, shown to be viable on an industrial scale as well, represents a promising means of treating the large quantities of problematic, chrome-bearing leather waste generated by commercial tanneries. The use of alkaline tannery effluents as alternative media to fresh water and lime (or any other suitable alkaline reagent) is particularly attractive in that it allows use to be made of a waste medium generated in large quantities by tanneries, and one which is therefore readily available for use in the treatment programme proposed in this study.

The fundamental importance of the alkaline hydrolysis stage is borne out by the fact that only 24% of the chromium was recovered from wet blue shavings by acid wash treatment without the benefit of preceding alkaline hydrolysis (Chapter 3). Very much higher, and in some cases even 100%, chromium recovery was possible from similar solid wastes after incubation in the alkaline effluents for periods as low as 5 minutes (Chapters 3–4). This was also evident in the industrial-scale investigations utilising wet blue shavings (Chapter 5). Furthermore, in addition to chromium recovery, substantial solubilisation of the hide protein was also possible, but only after much longer hydrolysis periods, and provided the suggested loading ratio (effluent:shavings) of approximately 20:1, or less, was adhered to. Two important problems associated with the disposal of tannery solid wastes can therefore be effectively and economically addressed, namely the volume of solid waste produced (can be reduced by protein solubilisation) and the presence of chromium (can now be removed for potential reutilisation).

The overall treatment programme can be explained in terms of two fundamental chemical principles. The first principle relates to differences in the relative susceptibility of co-ordinate covalent bonds and covalent bonds to alkaline hydrolysis, and the second involves the chemical behaviour of chromium under different pH conditions. The high concentrations of hydroxyl ions present in the tannery effluents initially effect rapid cleavage of the weaker co-ordinate covalent bonds between the chromium salts and the side-chain carboxyl groups of the leather protein. The extremely high affinity of trivalent chromium in a solution for hydroxide ions (Thorstensen, 1993)

and the high pH of the hydrolysis medium then leads to precipitation of the chromium as the hydroxide with very little chromium, usually less than the recommended discharge limit of 0.5mg.L^{-1} (Rawlings *et al*, 1987) remaining in the protein-containing supernatant. The chromium can then be recovered from the dried solid residue as the soluble sulphate by leaching the residue with a dilute solution of sulphuric acid. This is possible since trivalent chromium is soluble in aqueous media with a pH below 4 (Thorstensen, 1993). The precipitation of chromium under alkaline conditions, a process initially utilised in the treatment and chromium recovery programmes of tannery liquid wastes (Tsotsos, 1986; Rajamani *et al*, 1992), has now been successfully applied to the solid wastes as well.

Solubilisation of the solid wastes, on the other hand, required cleavage of the much more stable peptide (amide) bonds of collagen. Much longer hydrolysis periods and higher temperatures were therefore required for effective proteolysis leading to the formation of small, soluble peptide fragments and possibly even the constituent amino acids. The higher stability of the covalent amide bonds accounts for the observed detanning of the solid wastes before substantial protein solubilisation was evident. This was particularly evident where wet blue shavings were utilised as the solid substrate.

6.2. The suitability of tannery effluents as hydrolysis media.

While other alkaline reagents (e.g. sodium hydroxide, magnesium oxide (Lee, 1986), sodium carbonate and bicarbonate (Rajamani *et al*, 1992), amongst others (Langerwerf, 1985) are possible alternatives for use in the hydrolytic stage, independent studies have shown that Ca(OH)_2 , conveniently also the alkaline agent present in high concentration in the tannery effluents investigated, consistently produces a dense chromium precipitate with good settling characteristics when added to chromium solutions (Langerwerf, 1985). Furthermore, in suitable climatic conditions, the precipitate can be easily dewatered on drying beds and will therefore not require the utilisation of expensive mechanical dewatering equipment to partially dry the residue prior to acid wash or to reduce the volume of the chromium precipitate for transport to such treatment facilities.

Comparison of results from the investigations using fresh water and lime (Chapter 3) with those from the preliminary investigations using the three alkaline tannery effluents (Chapter 4) showed that chromium recovery was essentially unaffected when fresh water and lime was replaced by any one of the three effluents. Protein solubilisation, on the other hand, was reduced, albeit slightly for the wash and combined effluents, and more significantly for the unhairing effluent. The latter result is thought to be due to the high protein concentration of the unhairing effluent

prior to hydrolysis, which restricted the capacity of the effluent for further protein uptake during the alkaline hydrolysis stage. The wash and combined effluents therefore represent acceptable alternative media to lime-supplemented fresh water for both protein solubilisation and chromium recovery purposes, while the unhairing effluent can be considered effective only for the purposes of chromium recovery. The slightly reduced capacity of the wash and combined effluents for protein solubilisation is a small price to pay for the lime and fresh water savings derived. The water saving, in particular, is significant since the numerous washes, rinses and soaks required for the preparation of hides for tanning render tanneries water-intensive industries (Leather, 1991), and further substantial water demands for waste treatment programmes could be considered unfavourable.

6.3. Chromium recycling.

Extensive investigations carried out in the past have shown that utilisation of recycled chrome liquors does not have any apparent detrimental effect on the quality of the final leather produced, provided the correct basicity and chromium content of the recycled chrome-tanning liquor is adhered to (Slabbert and Boast, 1981; Gaughofer, 1990). Likewise, reutilisation of the chromium recovered from solid wastes should not detrimentally affect the quality of the final leather produced. Taylor *et al* (1990), using an enzyme-assisted simulated alkaline hydrolysis process, removed the chromium from tannery solid wastes and suggested that it could either be used directly in the pickle step or, alternatively, could be precipitated from the acid solution and used to make up the tan. The chromium recovered in this process, using a similar recovery programme, should offer the same potential for reuse and the same significant cost savings. The concentration of acid selected for the acid wash procedure should be such that solubilisation of organic materials is minimised, while chromium solubilisation from the solid residue is maximised. Too high an organic content in chromium tanning solutions may have a possible adverse affect on subsequent leather quality (Russell, 1993). A heavily protein-contaminated acid-chromium solution would necessitate precipitation of the chromium as the hydroxide from the proteinaceous material, with the associated increases in process time and cost. This study utilised a 1M sulphuric acid solution and a leaching period of 8 hours. Muralidhara *et al* (1982) showed that no additional chromium was recovered when the acid wash period was extended beyond approximately 8 hours.

6.4. Effect of alkaline hydrolysis on the chemical composition of the effluents.

The alkaline effluents utilised in these investigations, particularly the unhairing effluent, are problematic to tanneries and invariably require extensive treatment (Van Vlimmeren and Van Meer, 1974). The lime content, reduced by this treatment process, is objectionable because it

combines with carbon dioxide, produced during biological decomposition, to form calcium carbonate, which in turn may form a hard incrustation which can clog sewers (Tsotsos, 1986). The above treatment process has beneficial effects on the effluents in two other important ways: Firstly, conversion of the sulphide present to sulphate is enhanced, and secondly, any chromium present in the effluent is reduced. Sulphide is a particularly obnoxious and dangerous contaminant. Apart from its foul odour and toxicity, the accumulation of sulphide gases can cause crown corrosion of sewer pipes since anaerobic bacterial activity can lead to the formation of hydrogen sulphide gas, which in turn can be converted to corrosive sulphuric acid by the action of aerobic bacteria (Hammer, 1977). Sulphide also has detrimental effects on the microbial populations of biological treatment facilities such as activated sludges (Tsotsos, 1986). The most commonly employed method for reducing the sulphide content of tannery effluents involves aeration in the presence of a manganese catalyst (Shuttleworth, 1977).

The presence of chromium in the crude alkaline effluents (due to contamination from residual chromium-tanning liquors) merits further discussion since these effluents are usually treated biologically prior to discharge. Whilst some researchers claim that chromium salts exert a detrimental effect on biological treatment systems (Tsotsos, 1986), others refute this standpoint based on the fact that trivalent chromium is unable to cross biological membranes and, furthermore, at the slightly basic pH at which the activated sludge process operates (pH 7.5–8.0), the chromium should be precipitated from solution (Bailey *et al*, 1970). However, the resultant sludge produced will contain chromium which limits its marketability as a fertiliser or animal feed supplement (Shuttleworth, 1977). Since the reaction conditions of alkaline hydrolysis favour chromium precipitation, significantly reduced quantities of chromium are now likely to enter the biological treatment plant. Although the volume of final effluent discharged after the treatment programme will, at most, represent only a small percentage of the total alkaline effluents requiring treatment, any reduction in the chromium content of the pooled alkaline effluents, however small, will have a direct bearing on the chromium content of the resultant wastewater treatment sludges produced.

The organic content of the final effluent, arising from protein solubilisation, can be addressed by standard biological treatment processes. In those instances where the organic content is very high, such as would occur after extensive protein solubilisation, pooling of the protein-loaded effluent with the large volumes of alkaline effluents discharged from the tannery should dilute the effluent sufficiently to enable successful treatment.

6.5. Comparison with other proposed treatment programmes.

An effluent-based treatment programme possesses a number of advantages over the other proposed solid waste treatment processes outlined in Chapter 1. It does not convert the chromium to the hexavalent form, as occurs with incineration, thereby avoiding the need for a costly reduction extraction step to recover the chromium in a reusable form, but instead requires only a simple acid leaching procedure. Pyrolysis does not oxidise the chromium, but still requires operating temperatures in the range of 300-600°C. The effluent-based process requires temperatures of only 70°C for optimum solubilisation with comparatively high chromium recovery possible at even lower temperatures (i.e. 50°C). Furthermore, this process is more flexible than incineration and pyrolysis in that the degree of protein degradation can be controlled. It permits high chromium recovery at low temperatures (e.g. 50°C) and short run times with low protein solubilisation, and at progressively higher operating temperatures, protein solubilisation increases allowing the tannery to control the amount of residual (chrome-free) collagen. It may even be possible to tailor the process to exactly match the requirements of the by-product market for chrome-free collagen (e.g. cosmetic, food and animal feed supplements). Alternatively, the now chrome-free solid waste can be safely disposed of to landfill, if this option is available and if the organic content of the material is not an issue. The previously reported alkaline hydrolysis procedures, be they enzyme-assisted (Taylor *et al*, 1990) or enzyme-independent (Alves dos Reis and Beleza, 1991a), utilise fresh water supplemented with lime which will place a high demand on water resources should these processes be implemented on an industrial scale. The use of proteolytic enzymes to aid protein breakdown would further contribute to costs.

An alternative option would be to use a process based on acid instead of alkaline hydrolysis. However, hydrolysis under acidic conditions is not cost-effective (Bataille *et al*, 1983), particularly on an industrial scale. It would also lead to chromium co-solubilising with the protein instead of precipitating, and would therefore require a subsequent step to precipitate the chromium from solution, preventing direct recycling of the chrome-acid liquors. The alkaline hydrolysis process also allows for easier transportation of the chromium-containing cake should facilities not be available on site for chromium recovery. Vast volumes of a chromium-containing liquid are far more difficult and costly to transport than a concentrated, partially dried solid residue.

6.6. Cost assessment.

A detailed comparison of the expenses incurred in the disposal of solid wastes to landfill, as opposed to the adoption of the proposed effluent-based treatment process, was not undertaken. Clearly, costs will vary according to factors such as the stringency of disposal regulations, the quantity of solid wastes produced; specific cartage, landfill, labour, and raw materials costs, and

the availability of space and facilities for the implementation of the process, to mention but a few. However, it is important that some indication of the likely costs or areas of cost-saving involved be highlighted since it is likely that many tanneries may consider adopting this option in the light of impending stricter legislation, spiralling landfill costs and the need for an effective treatment programme for their solid wastes. Therefore, the most obvious areas of cost saving and expense will be emphasised, using illustrative costs supplied courtesy of Exotan (Pty) Ltd, Port Elizabeth, which were considered relevant at time of print.

Several obvious areas of cost savings and advantage would be derived from implementation of the proposed treatment process, not to mention the goodwill generated for the company by the adoption of a more environmentally friendly waste protocol. Firstly, an alkaline effluent produced on the premises would be used as the hydrolytic medium, instead of fresh water and lime. Secondly, utilisation of existing tannery facilities, for example, steam-heated fat-pots, pumping machinery, flexible piping *etc.*, would obviate the need for expensive capital outlays. The present cost of steam heating at Exotan (Pty) Ltd is approximately R 10.00 per hour, inclusive of labour, heating and maintenance costs (Hobson, 1993).

Adoption of the optimum operating conditions suggested in Chapter 5 (i.e. 100kg shavings, 100°C for 2 hours), assuming one treatment cycle per day, would incur heating costs of *ca.* R 400.00 per month. Thirdly, climatic conditions in Southern Africa favour drying of the hydrolysed solid residue on conventional drying beds, the only cost incurred here, being that of labour. Where adequate space is not available, or where climatic conditions are not conducive to such open air drying, mechanical equipment would need to be employed (e.g. a centrifuge or filter press), at obvious additional expense. The costs of acid washing the air-dried residue and chromium recycling could be offset by revenues generated from the sale of chrome-free collagen to by-product industries and the cost savings on replenishment of the chromium stock with recycled chromium. Disposal costs for the remaining unwanted chrome-free solid material, could also be further reduced if the hydrolysis process were tailored to further enhance solubilisation.

Solid wastes (wet blue shavings, wet blue splits and finished leather trimmings) at the former tannery are currently disposed of to landfill. A rented "dry waste" container (15m³), supplied by a waste removal agency, is kept on the premises of the tannery for removal when full. The total monthly cost for this service, inclusive of rental, cartage and landfill disposal, for approximately 60m³ (3 500–4 000kg) of dry solid waste, is presently approximately R1 500.00 (Hobson, 1993). It should be noted that disposal of a similar quantity of waste to landfill in European countries is likely to be very much more expensive, where suitable landfill sites are scarce and the regulations more stringent.

6.7. Concluding remarks.

No currently known alternative tanning agent is competitive with chromium in terms of leather quality and economics (Darrie, 1991). As a result, the tanning industry is very reluctant to change to an alternative tanning agent. The treatment process proposed in this study, coupled with the accepted policy of recycling chromium from tanning liquors, now provides the means whereby tanneries can justify the continued use of chromium as a tanning agent since it could virtually eliminate the disposal of chromium-containing solid wastes from the tannery.

The simplicity of the procedure ensures that its operation will require very little expertise and, provided treatment is carried out according to the guidelines suggested in Chapter 5 (temperature, incubation period and loading ratio), it is flexible enough to allow for chromium recovery with or without advanced protein solubilisation, according to the needs of the tannery. The adoption of any treatment programme for solid tannery wastes, such as the one proposed in this study, will depend on the legislative requirements of the country concerned and its economic viability. Tanneries in those countries where legislation is still lenient may well continue to dispose of their solid waste to landfill. However, this process may well provide the means whereby tanneries faced with particularly strict legislation can continue to be economically viable, or in those cases where hazardous landfill sites for chromium disposal are unavailable. In addition, it has the potential to bring tanneries one step closer to the idealised closed-circuit tannery where no chromium-contaminated material, other than the finished product, will go to waste. Its adoption would also allow the tanning industry to move away from a reactive approach, where compliance with existing environmental legislation is seen as the end goal, to a more innovative and proactive approach to waste management, comfortably ahead of legislative requirements.

CONCLUSION

1. It has been confirmed that wet blue shavings can be dechromed by simple acid leaching of the solid residue remaining following hydrolysis of the shavings in an alkaline medium consisting of fresh water and lime. In addition to detanning, the alkaline conditions also effected substantial solubilisation of the leather protein, but at a slower rate. The conditions under which hydrolysis should be conducted to ensure a supernatant containing $< 0.5 \text{ mg.L}^{-1}$ of chromium whilst optimising both chromium recovery from the solid residue and solubilisation of the leather collagen, were found to be:
lime — 10% w/w; temperature — 70°C; hydrolysis period — 12 hours.
2. Three alkaline tannery effluents *viz.* an unhairing, an unhairing wash and a combined process effluent, were investigated and found to be effective substitute hydrolysis media for fresh water and lime. The wash and combined effluents were found to be suitable media if both chromium recovery and extensive solubilisation of wet blue shavings is the objective, but the unhairing effluent was found to be suitable only for chromium recovery purposes. The conditions under which hydrolysis should be conducted to optimise both chromium recovery and solubilisation of the collagen in the wash or combined process effluent were determined to be: *temperature — 70°C; hydrolysis period — 6 hours.*
3. Ten-fold scale-up using either fresh water/lime or an effluent as the hydrolysis medium did not diminish the efficiency of the process, and it was also successfully conducted on wet blue shavings on an industrial scale. The following parameters were determined to be optimum on an industrial scale: *temperature — 70°C or higher; hydrolysis period — 2 hours (dechroming) or 6 hours (solubilisation and dechroming); loading ratio — 20:1 (medium:shavings).*
4. The recovery of chromium from, and solubilisation of, wet-blue splits and leather trimmings was less successful, however it is concluded that radical size-reduction of these leather wastes, e.g. shredding, would result in successful treatment.
5. Overall, the process shows great potential as a means of successfully treating the large quantities of problematic chrome leather waste generated by tanneries. The hydrolysis process also has the added benefit that, in addition to reducing the lime content of the effluent, the levels of chromium and sulphide in the initial effluents are also beneficially reduced.

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APPENDICES

APPENDIX I

(a) CHROMIUM.

Outline of method.

The chromium in the sample is converted to the hexavalent form and titrated against ferrous ammonium sulphate (FAS) in the presence of *N*-phenylanthranilic acid indicator.

Reagents.

- a. *perchloric/sulphuric acid mixture*: add 70mL of 98% H_2SO_4 to 230mL of 60% perchloric acid (HClO_4).
- b. *ferrous ammonium sulphate, 0.1N*: dissolve 250g of FAS ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) in 5L of distilled water. Warm if necessary. After cooling, add 100mL of concentrated H_2SO_4 .
- c. *N-phenylanthranilic acid indicator*: dissolve 2g of sodium carbonate (Na_2CO_3) in 20mL of distilled water. Add 1.07g of phenylanthranilic acid and dilute to 500mL with distilled water.
- d. *concentrated nitric acid.*
- e. *sulphuric acid, 1:1.*
- f. *potassium dichromate solution, 0.1N*: dissolve 4.904g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in distilled water and dilute to 1L (Vogel, 1961).

Procedure.

1. Place a suitable sample aliquot (20-50mL (liquid samples) or about 0.5g (solid samples)) into a 200mL kjeldahl flask, or similar vessel.
2. Add 5mL of concentrated HNO_3 , followed by 15mL of the $\text{HClO}_4/\text{H}_2\text{SO}_4$ mixture. The volume of HNO_3 can be varied slightly but not the volume of the $\text{HClO}_4/\text{H}_2\text{SO}_4$ mixture.
3. Heat the flask gently under a fume hood until most of the organic matter has been decomposed, as indicated by the lessening in the evolution of brown nitrous fumes. Then heat to boiling until all the particles of carbon have disappeared and until the colour of the solution changes from green to orange. Boiling must not be continued for more than 1 minute after this change.
4. When cool, dilute the sample mixture to about 100mL with distilled water.
5. Boil for a further 10 minutes to remove any free chlorine (until about 25mL remains in the flask). Allow to cool.
6. Determine the chromium concentration in a manner according to the concentration perceived to be present. High chromium concentrations are determined by titration; low chromium concentrations, by atomic absorption spectrophotometry.

A. Chromium determination by TITRATION.

7. Wash the above cooled sample mixture (from step 5) into Erlenmeyer flasks, with distilled water.
8. Add 4 drops of *N*-phenylanthranilic acid indicator solution and titrate with 0.1N FAS to the end point. Colour change - orange to green.

Standardisation of FAS.

1. To a flask, add 5mL of H₂SO₄ (1:1) and 25mL of 0.1N K₂Cr₂O₇ solution. Dilute to about 100mL with distilled water.
2. Add 4 drops of *N*-phenylanthranilic acid indicator and titrate with 0.1N FAS. Colour change- orange to green.
3. Determine factor "f" as follows:

$$f = \frac{25}{v}$$

where:

- f = factor for FAS (see following equation)
t = titre of FAS (mL)

Calculation.

$$\% \text{Cr}_2\text{O}_3 = \frac{t \times f(\text{FAS}) \times 0.001267 \times 100 \times 2}{w/a}$$

$$\% \text{Cr} = \% \text{Cr}_2\text{O}_3 \times 0.6842$$

$$\text{mg.L}^{-1} \text{Cr} = \% \text{Cr} \times 10\,000$$

where:

- Cr₂O₃ = chromium trioxide
t = titre of FAS (mL)
f = factor for FAS
w = sample weight (g)
a = sample aliquot (mL)
Cr = chromium (as total chromium)

B. Chromium determination by ATOMIC ABSORPTION SPECTROPHOTOMETRY.

7. Wash the above cooled sample mixture (from step 5) into a 50mL volumetric flask with distilled water and dilute to 50mL.
8. Determine the chromium concentration by atomic absorption spectrophotometry.

Calculation.

$$\% \text{ Cr} = \frac{r \times v \times 100}{10^6 \times a}$$

$$\text{mg.L}^{-1} \text{ Cr} = \% \text{ Cr} \times 10\,000$$

where:

Cr = chromium (as total chromium)

r = reading on atomic absorption spectrophotometer (in mg.L⁻¹)

v = final volume of diluted sample (mL)

a = sample aliquot (mL)

(b) ALKALINITY.

Outline of method.

The alkalinity of a water refers to the quantitative capacity of the water to react with a strong acid to a designated pH. The hydroxyl ions, present in the sample as a result of dissociation or hydrolysis of solutes, are neutralised by additions of standard acid. Alkalinity is thus dependent on the end point pH used (*Standard Methods for the Examination of Water and Waste-Water*, 1981).

Reagents.

a. *Indicator solutions:*

Phenolphthalein: dissolve 0.5g of phenolphthalein in 50mL of 95% ethyl alcohol and add 50mL of distilled water.

Methyl orange: dissolve 0.1g of methyl orange in 200mL of distilled water.

b. *standard sulphuric or hydrochloric acid, 0.1N.*

Procedure.

1. To a 50mL sample aliquot, add 1-2 drops of phenolphthalein.
2. If a pink colour develops, titrate with standard HCl to pH 8.3. At this pH phenolphthalein changes from pink to colourless. Record the titre (P).
3. Add a few drops of methyl orange and titrate until pH 3.7 is reached. Methyl orange will change from orange to red at pH 4.3 (ie. before the selected end point pH of 3.7 is reached). Record the total titre (T).

Calculation.

$$\text{mg.L}^{-1} \text{CaCO}_3 = \frac{t \times 1000}{a}$$

where:

- CaCO₃ = calcium carbonate
t = titre of acid (mL)
a = sample aliquot (mL)

(c) CHEMICAL OXYGEN DEMAND (COD).

Outline of method.

The COD is a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. Most types of organic matter are oxidised by a boiling mixture of chromic and sulphuric acids. A sample is refluxed in a strongly acid solution with a known excess of K₂Cr₂O₇. After digestion the remaining unreduced K₂Cr₂O₇ is titrated with FAS. The amount of K₂Cr₂O₇ consumed is determined and the amount of oxidisable organic matter calculated in terms of oxygen equivalent (*Standard Methods for the Examination of Water and Waste-Water*, 1981).

Reagents.

- a. *standard potassium dichromate, 0.25N; (stock solution):* dissolve 12.259g of K₂Cr₂O₇, (primary standard grade, previously dried at 103°C for 2 hours), in distilled water and dilute to 1 000mL.
(working solution): dissolve 7.5g of silver sulphate (Ag₂SO₄) in 250mL of K₂Cr₂O₇ (stock solution). Add 750mL of concentrated H₂SO₄. This solution is referred to as the digestion mixture.
- b. *standard ferrous ammonium sulphate, 0.1N:* dissolve 39g of FAS in a little distilled water. Add 20mL of concentrated H₂SO₄, cool, and dilute to 1 000mL with distilled water. This solution must be standardised daily against standard K₂Cr₂O₇ solution (see standardisation of FAS solution below).
- c. *ferroin indicator solution:* dissolve 1.485g of 1,10-phenanthroline monohydrate and 0.695g of ferrous sulphate (FeSO₄.7H₂O) in distilled water and dilute to 1 000mL.
- d. *mercuric sulphate (HgSO₄):* analytical-reagent grade crystals.

Apparatus.

Reflux apparatus: consisting of Erlenmeyer flasks with ground-glass necks and jacket condensers with ground-glass joints. The hot plate must have sufficient power to produce at least 1.4W/cm² of heating surface, or equivalent (*Standard Methods for the Examination of Water and Waste-Water*, 1981).

Standardisation of FAS solution.

1. Dilute 10mL of standard 0.25N K₂Cr₂O₇ solution to 100mL (ie. 0.025N K₂Cr₂O₇) with distilled water.
2. Add approximately 130mL of 9N H₂SO₄.
3. Add 4 drops of ferroin indicator and titrate with FAS solution to the end point. Colour change - blue-green to orange-red.
4. Determine the normality of the FAS solution as follows:

$$N = \frac{0.25}{t}$$

where:

N = normality of FAS solution
t = titre of FAS solution (mL)

Procedure.

1. Place 20mL of the sample, or a suitable dilution thereof, in a refluxing flask containing several glass beads.
2. Add 1g of HgSO₄, followed by 40mL of digestion mixture. The development of a green colour indicates further dilution of the sample is necessary.
3. Dilute the sample mixture to 120mL with distilled water. Mix. CAUTION: *The reflux mixture must be thoroughly mixed before applying heat, to prevent local heating of the flask bottom and a possible blowout of the flask contents.*
4. Reflux for 2 hours. Cool, and wash down the condenser with distilled water.
5. Cool samples to room temperature.
6. Add 4 drops of ferroin indicator and titrate the excess K₂Cr₂O₇ with standard FAS solution. The colour change is sharp, going from blue-green to reddish brown, and should be taken as the end point although the blue-green colour may reappear within minutes.
7. In the same manner, reflux and titrate a blank sample containing the reagents and a volume of distilled water equal to that of the sample.

Calculation.

$$\text{mg.L}^{-1} \text{ COD} = \frac{(A - B) \times N \times 8000}{a}$$

where:

- COD = chemical oxygen demand
A = titre of FAS solution used for blank (mL)
B = titre of FAS solution used for sample (mL)
N = normality of FAS solution
a = sample aliquot (mL)

(d) PERMANGANATE VALUE (PV)

Outline of method.

The PV is a measurement of the "oxygen absorbed" by a water sample following addition of an oxidising agent, viz. potassium permanganate, and titration with sodium thiosulphate.

Reagents.

a. *potassium permanganate solution, 0.0125N; (stock solution):* dissolve 8g of potassium permanganate (KMnO_4) in 1 000mL of hot distilled water in a large beaker covered with a clock glass, preferably heating the solution to 90-95°C for 2-3 hours.

(working solution): dilute 50mL of the stock solution to 1 000mL with distilled water.

Set aside for several days in the dark to ensure complete oxidation of any organic matter and to allow any precipitated manganese dioxide to settle. Carefully decant or siphon off the supernatant liquid, avoiding disturbance of the sediment. Alternatively, filter the solution through a sintered glass funnel, through glass wool or through asbestos fibre previously digested with HNO_3 and HCl and then thoroughly washed with water; *do not filter through paper*. Dust or organic matter must not be allowed to contaminate the solution.

b. *sodium thiosulphate solution, 0.0125N:* dissolve 3.1g of sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 1 000mL of copper-free, freshly boiled and cooled distilled water. Add 3 drops of chloroform to stabilise the solution. Allow to stand for several days before use. This solution should be standardised against $\text{K}_2\text{Cr}_2\text{O}_7$ at frequent intervals (see standardisation of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ below). Store in an amber glass bottle with a rubber stopper and discard any solution remaining in the burette at the end of the day.

c. *standard potassium dichromate solution, 0.025N:* dissolve 1,226g of previously dried $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water and dilute to 1 000mL.

- d. *starch indicator, (stock solution)*: dissolve 6.7g of soluble starch and 40g of NaCl in 200mL of distilled water. Add 20mL of 18N glacial acetic acid (CH_3COOH) and boil for 5 minutes.
(working solution): dilute 10mL of the stock solution to 200mL with distilled water.
- e. *dilute sulphuric acid, 9N*.
- f. *potassium iodide (KI)*: reagent grade.

Standardisation of $\text{Na}_2\text{S}_2\text{O}_3$ solution.

1. Dissolve 1g of KI, (free from iodate), in 75mL of distilled water.
2. Add 4mL of 9N H_2SO_4 , followed by 10mL of 0.025N $\text{K}_2\text{Cr}_2\text{O}_7$. Allow to stand in the dark for 5 minutes.
3. Add 120mL of distilled water and titrate with 0.0125N $\text{Na}_2\text{S}_2\text{O}_3$ solution to a pale straw colour. Add starch indicator and titrate until colourless.
4. Determine the normality of the $\text{Na}_2\text{S}_2\text{O}_3$ solution as follows:

$$N = \frac{0.25}{t}$$

where:

$$N = \text{normality of } \text{Na}_2\text{S}_2\text{O}_3 \text{ solution}$$

$$t = \text{titre of } \text{Na}_2\text{S}_2\text{O}_3 \text{ solution (mL)}$$

Procedure.

1. Into a clean glass-stoppered bottle, place 10mL of 9N H_2SO_4 and 50mL of 0.0125N KMnO_4 .
2. Add 100mL of the sample, or a suitable dilution thereof, and mix immediately by gentle rotation of the bottle. Dilute the contents with distilled water to approximately 200-250mL. If the contents become colourless after addition of the sample, greater dilution of the sample is necessary.
3. Maintain the sample contents at 27°C for 4 hours, by placing the sample bottles in a constant temperature water bath. Remix the contents after 1 hour if the sample contains much suspended matter.
4. After 4 hours add 0.5g of KI and mix.
5. Titrate immediately with 0.0125N $\text{Na}_2\text{S}_2\text{O}_3$ solution, adding 2mL of starch solution towards the end of the titration (a pale straw yellow colour). Titrate until the blue colour just disappears. Ignore any blue colour which may return upon standing.
6. Prepare a blank determination in the same manner as above, using 100mL of distilled water in place of the sample.

Calculation.

$$\text{mg.L}^{-1} \text{ PV} = \frac{(A - B) \times N \times 8000}{a}$$

where:

- PV = permanganate value
A = titre of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for blank (mL)
B = titre of $\text{Na}_2\text{S}_2\text{O}_3$ solution used for sample (mL)
N = normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution
a = sample aliquot (mL)

(e) CHLORIDE.

Outline of method.

In a natural or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed (*Standard Methods for the Examination of Water and Waste-Water*, 1981).

Reagents.

- a. *5% potassium chromate indicator solution:* dissolve 50g of potassium chromate (K_2CrO_4) in a little distilled water. Add silver nitrate (AgNO_3) solution until a definite red precipitate is formed. Allow to stand for 12 hours, filter and dilute to 1 000mL with distilled water.
- b. *silver nitrate solution, 0.1N:* dry some finely powdered analytical reagent AgNO_3 at 120°C for 2 hours and allow to cool in a covered vessel in a desiccator. Weigh out accurately 8.496g ‡, dissolve it in distilled water and make up to 500mL. Alternatively, about 8.5g of the pure, dry AgNO_3 may be weighed out accurately, dissolved in 500mL of distilled water and the exact normality computed from the weight of the AgNO_3 employed (Vogel, 1961).
‡ this weight should be multiplied by the purity factor of the analytical reagent AgNO_3 eg. by 1/0.999 (Vogel, 1961).
- c. *concentrated nitric acid.*
- d. *sodium acetate ($\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$):* general purpose reagent.

Procedure.

1. Pipette a suitable sample aliquot (1-10mL) into 50mL of deionised water.
2. Add 3 drops of concentrated HNO_3 and boil for 5 minutes. The HNO_3 removes the sulphide which interferes with the titration. Cool slightly.

3. Add approximately 2g of $\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ and boil for 5 minutes. $\text{NaCH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ removes the excess HNO_3 . Cool slightly. If the volume remaining is less than 50mL add deionised water.
4. Titrate with 0.1N AgNO_3 solution, using 5 drops of 5% KCrO_4 solution as the indicator. Colour change - yellow to brown-red.

Calculation

$$\% \text{ Cl} = \frac{t \times f \times 0.003546 \times 100}{a}$$

$$\text{mg.L}^{-1} \text{ chloride} = \% \text{ Cl} \times 10\,000$$

where:

- Cl = chloride
 t = titre of AgNO_3 solution (mL)
 f = factor for AgNO_3 solution
 a = sample aliquot (mL)

Determination of factor 'f':

Factor $f = 1$ when the AgNO_3 solution is made up to exactly 0.1N.

(f) SULPHIDE.

Outline of method.

The sulphide solution is titrated with standard potassium ferricyanide solution in the presence of a ferrous dimethylglyoxime ammonia complex. The sulphide is oxidised to sulphur. Sulphite interferes and must be precipitated with barium chloride. Thiosulphate is not titrated under the conditions of the determination.

Reagents.

- a. *standard potassium ferricyanide solution, 0.1N:* dissolve 32.925g of potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) in 1 000mL of distilled water. This solution must be kept in the dark.
- b. *ammonium chloride buffer:* dissolve 200g of ammonium chloride (NH_4Cl) in a little distilled water. Add 200mL of ammonia (Specific gravity 0.880) and dilute the contents to 1 000mL with distilled water.

- c. *barium chloride solution*: dissolve 12.5g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 1 000mL of distilled water. 10mL of this solution will precipitate the equivalent of about 0.3g of sodium sulphite.
- d. *indicator solution*: add 10mL of 0.6% ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 0.5mL of concentrated H_2SO_4 to 50mL of 1% dimethylglyoxime in ethanol.

Procedure.

1. Filter the sample aliquot rapidly (allow minimum aeration) through glass wool or a coarse filter paper to remove the suspended material.
2. To a stoppered flask, add 20mL of buffer, 1mL of indicator solution, and excess BaCl_2 solution up to a maximum of 25mL.
3. Add a suitable aliquot of the sample containing, if possible, between 0.04 and 0.08g of sodium sulphide. Stopper the flask and allow to stand for 1 minute to precipitate the sulphite.
4. Titrate the sample solution with the standard $\text{K}_3\text{Fe}(\text{CN})_6$ solution until the pink colour is destroyed. During titration the sample solution sometimes goes a dirty colour, but near completion the pink colour becomes more definite and disappears momentarily before the final end point is reached. The sample solution is titrated until there is no reappearance of the pink colour after 30 seconds.

Calculation.

$$\% \text{Na}_2\text{S} = \frac{t \times f \times 0.0039 \times 100}{a}$$

$$\text{mg.L}^{-1} \text{Na}_2\text{S} = \% \text{Na}_2\text{S} \times 10\,000$$

where:

- Na_2S = sodium sulphide
- t = titre of standard $\text{K}_3\text{Fe}(\text{CN})_6$ solution (mL)
- f = factor "f" (see determination of "f" above)
- a = sample aliquot (mL)

(g) SULPHATE.

Outline of method.

Sulphate is precipitated in an HCl solution, as barium sulphate, by the addition of BaCl₂. The precipitation is carried out near the boiling temperature. After a period of digestion, the precipitate is filtered, washed with water until free of chlorides, ignited, and weighed as barium sulphate (BaSO₄).

Reagents.

- a. *barium chloride solution:* dissolve 100g of BaCl₂·2H₂O in 1 000mL of distilled water. Filter through a membrane filter or hard-finish filter paper before use. 1mL is capable of precipitating approximately 40mg of sulphate.
- b. *hydrochloric acid, 75%.*

Procedure.

1. Adjust the pH of a suitable sample aliquot to pH 4.5 - 5.0, with 75% HCl (1-2mL HCl).
2. Heat the sample to boiling on a steam bath.
3. While stirring gently, slowly add warm BaCl₂ solution until precipitation of the BaSO₄ appears to be complete. Then add about 2mL of BaCl₂ solution in excess. If the amount of precipitate is small, add a total of 5mL of BaCl₂ solution.
4. Digest the precipitate at 80-90°C, preferably overnight, but for not less than 2 hours.
5. Filter the BaSO₄ at room temperature through an ashless filter paper. Wash the precipitate with several small portions of warm distilled water.
6. Transfer the filter and precipitate to a tared crucible and ignite at 600°C for 4 hours.
Do not allow the filter paper to flame.
7. Cool in a desiccator and weigh.

Calculation.

$$\text{mg.L}^{-1} \text{ sulphate} = \frac{w \times 411.6}{a}$$

where:

- w = weight of BaSO₄ (mg)
a = sample aliquot (mL)

(h) NITROGEN (FREE AND SALINE AMMONIA).

Outline of method.

The sample is distilled into a solution of boric acid containing mixed indicators. The ammonia in the distillate is determined titrimetrically with H₂SO₄.

Reagents.

- a. *boric acid solution:* dissolve 40g of boric acid (H₃BO₃) in 1 000mL of ammonia-free distilled water. The indicators (methyl red and methylene blue mix) are included in the H₃BO₃ solution.
- b. *caustic soda (sodium hydroxide) solution:* slowly add 5kg of solid caustic soda to 10.5L of distilled water. Stir well with cooling.
- c. *sulphuric acid:* the strength (normality) of the H₂SO₄ solution is dependent upon the concentration of ammonia perceived to be present. For low concentrations of ammonia, use a more dilute H₂SO₄ solution, and vice versa.

Procedure.

1. Place 50mL of the sample in a 500mL kjeldahl flask and dilute to 100mL with ammonia-free distilled water.
2. Add 100mL of caustic soda. This generates an alkaline solution to enable distillation of the ammonia.
3. Shake the mixture and distil immediately, as vigorously as possible. The distillation flask should be fitted with a splash head and vertical pyrex condenser. Distil into 50mL of H₃BO₃ solution. The outlet tip attached to the condenser must be submerged at least 2cm below the surface of the H₃BO₃ solution. Continue the distillation until approximately 150mL of distillate is collected.
4. Titrate the ammonia in the distillate against H₂SO₄, matching the end point with that of a blank containing the same amount of H₃BO₃ solution diluted to the same volume with carbon dioxide-free distilled water. Colour change - green to purple.

Calculation.

$$\%N = \frac{t \times 0.0017 \times 5 \times 100}{a}$$

$$\text{mg.L}^{-1} \text{ ammonia nitrogen} = \%N \times 10\ 000$$

where:

- N = nitrogen (as ammonia)
t = titre of H₂SO₄ solution (mL)
a = sample aliquot (mL)

Note.

- In the above equation: 0.5N H₂SO₄ = t
0.1N H₂SO₄ = t/5
0.05N H₂SO₄ = t/10

(i) NITROGEN (NITRATE).

Outline of method.

After the determination of ammonia nitrogen by the distillation method, the nitrates and nitrites in the residue are reduced by boiling with Devarda's alloy. The ammonia so produced is distilled over and determined by titration with H₂SO₄.

Reagents.

- a. All the reagents required for the determination of ammonia nitrogen plus:
b. Devarda's alloy: Nitrogen-free and fine enough to pass through a 200 mesh sieve

Procedure.

1. The ammonia is distilled off as described under "Nitrogen (free and saline ammonia) determination". Dilute the residue in the distillation flask to approximately 200mL with ammonia-free distilled water.
2. Add 1g of Devarda's alloy and distil into 50mL of H₃BO₃ solution. Devarda's alloy dissolves in caustic soda, releasing nascent hydrogen which reduces the nitrates and nitrites to ammonia. The nitrites oxidise readily, thus very little will be present.
3. Bubbles of gas will become visible as the distillation flask is heated. The heat must be turned down to avoid frothing and excessive spray formation upon commencement of boiling.
4. Boil the contents gently for 5-10 minutes, followed by vigorous boiling for a further 20 minutes, provided that the latter does not cause excessive frothing.
5. Continue the distillation until approximately 150mL of distillate is collected.
6. Titrate the ammonia in the distillate against H₂SO₄, matching the end point with that of a blank containing the same amount of H₃BO₃ solution diluted to the same volume with carbon dioxide-free distilled water. Colour change - green to purple.

Calculation.

$$\%N = \frac{t \times 0.0062 \times 5 \times 100}{a}$$

$$\text{mg.L}^{-1} \text{ nitrate nitrogen} = \%N \times 10\,000$$

where:

- N = nitrogen (as nitrate)
t = titre of H₂SO₄ solution (mL)
a = sample aliquot (mL)

Note.

- In the above equation: 0.5N H₂SO₄ = t
0.1N H₂SO₄ = t/5
0.05N H₂SO₄ = t/10

(j) TOTAL KJELDAHL NITROGEN (TKN).

Outline of method.

In the presence of H₂SO₄, potassium sulphate, and mercuric sulphate catalyst, the amino nitrogen of many organic materials is converted to ammonium sulphate. Free ammonia and ammonia nitrogen are also converted to ammonium sulphate (*Standard Methods for the Examination of Water and Waste-Water*, 1981). The addition of excess caustic soda liberates the ammonia which is distilled into a H₃BO₃ solution and titrated against H₂SO₄.

Reagents.

- a. All the reagents required for the determination of ammonia nitrogen plus:
- b. *digestion mixture*: dissolve 300g of potassium sulphate (K₂SO₄) and 30g of copper sulphate (CuSO₄.5H₂O) in a little distilled water, heating gently. Dilute to 3 750mL with further distilled water. Cool. Slowly add, with stirring, 1 250mL of concentrated H₂SO₄.
- c. *carborundum powder*.

Procedure.

1. To a 50mL sample aliquot in a 500mL kjeldahl flask, add 100mL of digestion mixture.
2. Place the flask in an inclined position and heat under a hood, or with suitable ejection equipment, to remove SO₃ fumes. Continue to boil briskly for about 60 minutes after the liquid becomes clear or nearly colourless. Allow the flask and contents to cool.

3. Dilute the sample mixture with 250mL of ammonia-free distilled water and add a few grains of carborundum powder.
4. Without mixing the contents, carefully add 100mL of caustic soda solution down the side of the flask.
5. Once the flask is connected to the distillation apparatus, carefully mix the contents and distil immediately into 50mL of H₃BO₃ solution. Continue the distillation until approximately 150mL of distillate is collected. Ensure that the outlet tip of the condenser is submerged at least 2cm below the surface of the H₃BO₃ solution at all times.
6. Titrate the ammonia in the distillate against H₂SO₄, matching the end point with that of a blank containing the same amount of H₃BO₃ solution diluted to the same volume with carbon dioxide-free distilled water. Colour change - green to purple.

Calculation.

$$\%N = \frac{t \times 0.0014 \times 5 \times 100}{a}$$

$$\text{mg.L}^{-1} \text{ nitrogen} = \%N \times 10\,000$$

where:

- N = nitrogen (as total nitrogen)
 t = titre of H₂SO₄ solution (mL)
 a = sample aliquot (mL)

Note.

- In the above equation: 0.5N H₂SO₄ = t
 0.1N H₂SO₄ = t/5
 0.05N H₂SO₄ = t/10

(k) SOAP, OIL AND GREASE.

Outline of method.

Dissolved or emulsified oil and grease is extracted from water by intimate contact with petroleum ether. The gain in weight of the tared distilling flask is due to the extracted soap, oil or grease in the sample (provided the organic solvent is free of residue).

Reagents.

- a. *petroleum ether*: (boiling point 40-60°C).
- b. *saturated salt (NaCl) solution*.
- c. *sodium sulphate (NaSO₄)*: anhydrous, crystalline.
- d. *hydrochloric acid, (1:1)*.
- e. *acetone*.

Procedure.

1. Acidify a 100mL sample aliquot with 1:1 HCl to pH 3 - 4.
2. Transfer the acidified sample to a separating funnel. Carefully rinse the sample flask with about 15mL of petroleum ether and add the ether washings to the separating funnel.
3. Add an additional 35mL of petroleum ether to the separating funnel. Preferably shake the contents vigorously for 2 minutes, but if it is suspected that a stable emulsion will form, shake gently for 5-10 minutes. Allow the ether layer to separate.
4. Transfer the solvent layer into a clean flask, capable of holding at least three volumes of solvent.
5. Carry out two further extractions on the aqueous layer, each with 50mL of petroleum ether. Combine the ether extractions.
6. Return the combined ether extractions to the separating funnel and wash with distilled water until acid free. Any emulsified material present can be dispersed with a little saturated salt solution.
7. Dry the ether extract over anhydrous NaSO₄ if a clear solvent layer cannot be obtained.
8. Drain the ether extract through a funnel containing solvent moistened filter paper (Whatman #40, or equivalent) into a tared distilling flask. Wash the funnel and filter paper with a small volume of fresh petroleum ether.
9. Distil off all but approximately 10mL of the ether extract, keeping the source of heat at about 70°C.
10. Complete the evaporation on a steam bath, adding about 2mL of acetone to remove moisture.
11. Dry the residue in an oven at 100°C for 1 hour. Cool in a desiccator and weigh.

Calculation.

$$\text{mg.L}^{-1} \text{ soap, oil or grease} = \frac{r \times 1000}{a}$$

where:

- r = residue weight (mg)
a = sample aliquot (mL)

APPENDIX II

Table I. Initial chromium content of the crude wet blue shavings utilised in each investigation as determined by mass balance calculation.

Nature of investigation	chromium content (%)
hydrolysis medium - fresh water	
optimisation of: degree of alkalinity	2.3
hydrolysis temperature	2.2
hydrolysis duration	2.3
scaled-up investigation	2.3
hydrolysis medium - unhairing effluent	
optimisation of: hydrolysis temperature	1.9
hydrolysis duration	1.6
hydrolysis medium - wash effluent	
optimisation of: hydrolysis temperature	2.4
hydrolysis duration	2.4
scaled-up investigation	2.4
hydrolysis medium - combined effluent	
scaled-up investigation	2.1
industrial scale; wet weight: 50kg	1.5
100kg	3.0
150kg	2.1
220kg	2.1

Table II. Comprehensive listing of the results obtained for the fresh water alkaline hydrolysis investigations (optimisation of % lime, hydrolysis temperature, hydrolysis period and scaled-up investigation).

		initial pH	final pH	solubilisation of shavings (%)	Cr content (supernatant) (mg.L ⁻¹)	Cr content (solid residue) (%)	Cr recovery (%)
lime optimisation	0	6.89 ± 0.13	4.46 ± 0.10	20.5 ± 0.4	0.30 ± 0.04	3.0 ± 0.1	45 ± 1
	4	10.44 ± 0.09	7.69 ± 0.03	20.3 ± 0.4	0.48 ± 0.01	2.6 ± 0.0	85 ± 2
	6	11.06 ± 0.07	8.55 ± 0.07	22.4 ± 1.8	0.41 ± 0.02	2.9 ± 0.1	88 ± 1
	8	11.17 ± 0.07	9.12 ± 0.05	40.4 ± 3.4	0.36 ± 0.01	4.0 ± 0.3	85 ± 3
	10	11.42 ± 0.05	10.10 ± 0.03	70.9 ± 2.2	0.36 ± 0.01	7.2 ± 0.1	85 ± 2
	12	11.56 ± 0.04	10.14 ± 0.03	71.1 ± 0.5	0.33 ± 0.01	7.4 ± 0.1	87 ± 2
temperature optimisation	50°C	11.13 ± 0.04	10.75 ± 0.02	13.9 ± 0.4	0.19 ± 0.01	2.6 ± 0.1	92 ± 1
	60°C	10.67 ± 0.09	10.39 ± 0.03	52.0 ± 0.9	0.43 ± 0.05	5.3 ± 0.2	98 ± 1
	70°C	10.50 ± 0.10	10.00 ± 0.05	71.9 ± 0.2	0.28 ± 0.01	8.4 ± 0.2	100 ± 1
	80°C	10.38 ± 0.04	9.62 ± 0.04	73.0 ± 1.3	0.49 ± 0.04	8.8 ± 0.3	100 ± 1
time optimisation	1 hour	10.63 ± 0.06	10.51 ± 0.14	34.7 ± 0.4	0.23 ± 0.01	3.6 ± 0.1	84 ± 3
	2 hour	10.84 ± 0.03	10.30 ± 0.04	44.3 ± 3.8	0.28 ± 0.02	4.3 ± 0.3	88 ± 2
	6 hour	10.79 ± 0.06	10.30 ± 0.13	64.3 ± 1.3	0.24 ± 0.03	7.1 ± 0.2	94 ± 2
	12 hour	10.83 ± 0.01	9.98 ± 0.09	69.8 ± 0.1	0.25 ± 0.01	8.0 ± 0.1	100 ± 1
	24 hour	10.72 ± 0.03	9.66 ± 0.13	71.5 ± 1.1	0.38 ± 0.03	8.4 ± 0.6	98 ± 1
scaled-up		10.61 ± 0.03	9.85 ± 0.07	70.0 ± 1.0	0.23 ± 0.02	8.1 ± 0.1	98 ± 2

Table III. Comprehensive listing of the results obtained for the unhairing effluent investigations (optimisation of hydrolysis temperature and hydrolysis period).

		initial pH	final pH	solubilisation of shavings (%)	Cr content (supernatant) (mg.L ⁻¹)	Cr content (solid residue) (%)	Cr recovery (%)
temperature optimisation	50	11.76 ± 0.02	11.59 ± 0.01	44.7 ± 8.2	0.44 ± 0.04	2.9 ± 0.1	74 ± 2
	60	11.50 ± 0.01	11.33 ± 0.03	40.1 ± 2.7	0.30 ± 0.06	3.1 ± 0.3	81 ± 2
	70	11.31 ± 0.02	10.68 ± 0.01	43.4 ± 0.5	0.31 ± 0.01	2.5 ± 0.1	95 ± 1
	80	11.29 ± 0.02	10.37 ± 0.04	31.1 ± 0.5	0.52 ± 0.03	2.7 ± 0.0	86 ± 2
	50 (control)	11.85 ± 0.02	11.74 ± 0.02	—	0.18 ± 0.03	—	—
	60 (control)	11.58 ± 0.03	11.46 ± 0.01	—	0.14 ± 0.01	—	—
	70 (control)	11.55 ± 0.01	11.02 ± 0.02	—	0.36 ± 0.02	—	—
	80 (control)	11.39 ± 0.01	10.87 ± 0.03	—	0.32 ± 0.02	—	—
time optimisation	1 hour	11.43 ± 0.01	11.25 ± 0.01	26.9 ± 1.1	1.08 ± 0.13	3.1 ± 0.1	83 ± 2
	2 hour	11.42 ± 0.03	11.19 ± 0.02	56.6 ± 5.3	0.38 ± 0.08	3.3 ± 0.1	85 ± 2
	6 hour	11.49 ± 0.03	11.08 ± 0.01	66.1 ± 0.2	0.29 ± 0.02	3.0 ± 0.1	66 ± 5
	12 hour	11.54 ± 0.01	10.93 ± 0.03	58.4 ± 1.2	0.21 ± 0.01	2.9 ± 0.01	76 ± 2
	24 hour	11.43 ± 0.02	10.42 ± 0.03	44.1 ± 1.2	0.25 ± 0.01	3.2 ± 0.1	75 ± 3
	1 hour (control)	11.56 ± 0.03	11.38 ± 0.02	—	0.27 ± 0.01	—	—
	2 hour (control)	11.50 ± 0.02	11.37 ± 0.02	—	0.26 ± 0.01	—	—
	6 hour (control)	11.57 ± 0.01	11.14 ± 0.02	—	0.17 ± 0.03	—	—
	12 hour (control)	11.64 ± 0.02	11.00 ± 0.03	—	0.06 ± 0.02	—	—
	24 hour (control)	11.56 ± 0.01	10.89 ± 0.01	—	0.10 ± 0.03	—	—

Table IV. Comprehensive listing of the results obtained for the wash effluent investigations (optimisation of hydrolysis temperature, hydrolysis period, and scaled-up investigation).

		initial pH	final pH	solubilisation of shavings (%)	Cr content (supernatant) (mg.L ⁻¹)	Cr content (solid residue) (%)	Cr recovery (%)
temperature optimisation	50	11.57 ± 0.01	11.04 ± 0.02	8.4 ± 1.7	0.53 ± 0.11	2.5 ± 0.1	100 ± 1
	60	11.48 ± 0.01	10.70 ± 0.01	49.5 ± 0.7	0.52 ± 0.03	5.7 ± 0.2	94 ± 1
	70	11.23 ± 0.01	10.16 ± 0.04	60.9 ± 1.0	0.04 ± 0.01	6.4 ± 0.1	92 ± 2
	80	11.20 ± 0.01	9.80 ± 0.01	61.3 ± 1.0	0.04 ± 0.01	6.8 ± 0.0	94 ± 1
	50 (control)	11.81 ± 0.02	11.72 ± 0.02	—	0.04 ± 0.03	—	—
	60 (control)	11.69 ± 0.01	11.52 ± 0.01	—	0.01 ± 0.01	—	—
	70 (control)	11.49 ± 0.01	11.13 ± 0.02	—	0.01 ± 0.02	—	—
	80 (control)	11.46 ± 0.02	10.99 ± 0.01	—	0.01 ± 0.02	—	—
time optimisation	1 hour	11.34 ± 0.04	10.98 ± 0.02	32.9 ± 1.7	0.61 ± 0.04	4.5 ± 0.2	84 ± 3
	2 hour	11.34 ± 0.04	10.85 ± 0.03	41.3 ± 2.5	0.76 ± 0.12	5.0 ± 0.1	89 ± 2
	6 hour	11.36 ± 0.04	10.71 ± 0.04	53.4 ± 1.3	0.15 ± 0.00	5.1 ± 0.0	82 ± 3
	12 hour	11.38 ± 0.02	10.58 ± 0.02	55.5 ± 0.9	0.08 ± 0.01	5.1 ± 0.1	87 ± 2
	24 hour	11.30 ± 0.01	10.07 ± 0.05	53.5 ± 0.5	0.19 ± 0.01	5.2 ± 0.1	84 ± 2
	1 hour (control)	11.56 ± 0.03	11.50 ± 0.02	—	0.04 ± 0.01	—	—
	2 hour (control)	11.64 ± 0.04	11.45 ± 0.03	—	0.08 ± 0.01	—	—
	6 hour (control)	11.66 ± 0.04	11.35 ± 0.04	—	0.03 ± 0.01	—	—
	12 hour (control)	11.58 ± 0.03	11.31 ± 0.02	—	0.01 ± 0.00	—	—
	24 hour (control)	11.57 ± 0.02	11.16 ± 0.03	—	0.01 ± 0.00	—	—
scaled-up (sample)		11.04 ± 0.02	10.32 ± 0.03	53.7 ± 0.1	0.18 ± 0.05	5.3 ± 0.2	91 ± 2
scaled-up (control)		11.19 ± 0.03	10.57 ± 0.02	—	0.04 ± 0.03	—	—

Table V. Comprehensive listing of the results obtained for the combined effluent bench-scale investigation (scaled-up investigation).

	initial pH	final pH	solubilisation of shavings (%)	Cr content (supernatant) (mg.L ⁻¹)	Cr content (solid residue) (%)	Cr recovery (%)
scaled-up (sample)	11.21 ± 0.03	10.57 ± 0.01	60.8 ± 0.0	0.13 ± 0.01	5.3 ± 0.0	91 ± 2
scaled-up (control)	11.32 ± 0.04	10.69 ± 0.02	—	0.10 ± 0.01	—	—

Table VI. Comprehensive listing of the results obtained for the combined effluent industrial-scale investigations (wet blue shavings).

wet weight of shavings (kg)	time (hours)	initial pH	solubilisation of shavings (%)	Cr content (supernatant) (mg.L ⁻¹)	Cr content (solid residue) (%)	Cr recovery (%)	size reduction (%)
50	0.08 (5 min)	11	30	0.30 ± 0.01	2.3 ± 0.1	96	—
	1	11	57	0.18 ± 0.06	3.4 ± 0.3	100	—
	2	11	65	0.17 ± 0.02	3.9 ± 0.1	100	—
	3	11	82	0.11 ± 0.01	4.1 ± 0.0	100	—
	4	11	54	0.22 ± 0.05	4.7 ± 0.0	100	—
	5	11	62	0.25 ± 0.04	4.2 ± 0.1	100	—
	6	11	65	0.14 ± 0.02	4.9 ± 0.1	99	—
100	0.08 (5 min)	11	5	0.25 ± 0.02	3.0 ± 0.1	88	11
	0.25 (15 min)	11	6	0.37 ± 0.04	3.0 ± 0.0	100	57
	0.50 (30 min)	11	7	0.33 ± 0.03	3.6 ± 0.0	100	68
	0.75 (45 min)	11	24	0.34 ± 0.02	4.0 ± 0.1	96	76
	1	11	30	0.19 ± 0.01	4.5 ± 0.1	99	80
	2	11	44	0.15 ± 0.02	5.6 ± 0.0	100	88
	3	11	51	0.25 ± 0.05	6.4 ± 0.1	100	87
	4	11	50	0.19 ± 0.01	6.5 ± 0.3	100	90
	5	11	57	0.17 ± 0.02	7.0 ± 0.0	98	92
	6	11	58	0.15 ± 0.01	6.7 ± 0.1	99	92

150	0.08 (5 min)	11	48	1.26 ± 0.04	2.4 ± 0.0	83	40
	0.25 (15 min)	11	10	0.34 ± 0.02	2.4 ± 0.1	76	32
	0.50 (30 min)	9	37	0.33 ± 0.03	2.5 ± 0.1	72	24
	0.75 (45 min)	9	29	0.35 ± 0.02	2.5 ± 0.0	79	18
	1	9	29	0.34 ± 0.01	2.5 ± 0.0	72	20
	2	8.5	28	0.31 ± 0.02	2.7 ± 0.1	68	31
	3	8.5	29	0.35 ± 0.01	2.9 ± 0.1	76	34
	4	8	36	0.34 ± 0.01	3.2 ± 0.0	75	48
	5	8	32	0.33 ± 0.01	3.5 ± 0.1	74	51
	6	8	42	0.41 ± 0.00	3.8 ± 0.0	68	67
220	0.08 (5 min)	10	16	0.73 ± 0.03	2.5 ± 0.0	97	21
	0.25 (15 min)	10	48	0.24 ± 0.05	2.5 ± 0.0	100	56
	0.50 (30 min)	10	84	0.25 ± 0.05	2.5 ± 0.1	98	88
	0.75 (45 min)	9	87	0.20 ± 0.01	2.4 ± 0.0	100	97
	1	9	37	0.31 ± 0.02	2.4 ± 0.1	100	43
	2	8.5	18	0.49 ± 0.06	2.5 ± 0.0	100	32
	3	8.5	18	0.47 ± 0.02	2.6 ± 0.1	93	37
	4	8	27	0.54 ± 0.03	2.8 ± 0.1	100	51
	5	8	30	0.55 ± 0.02	3.1 ± 0.2	100	69
	6	8	30	0.48 ± 0.03	3.2 ± 0.1	93	62

Table VII. Comprehensive listing of the results obtained for the combined effluent industrial-scale investigation (wet blue splits and finished leather trimmings).

Time (hours)	initial pH	Cr content (supernatant) (mg.L ⁻¹)	Cr content (solid residue)		Cr recovery	
			(%)		(%)	
0	—	—	3.0 ± 0.0	2.0 ± 0.1	34	10
0.08 (5 min)	12.5	0.39 ± 0.03	2.9 ± 0.0	2.2 ± 0.1	75	36
0.25 (15 min)	12	0.19 ± 0.01	3.0 ± 0.1	2.4 ± 0.0	74	51
0.50 (30 min)	12	0.15 ± 0.02	3.1 ± 0.0	2.9 ± 0.0	84	63
0.75 (45 min)	12	0.21 ± 0.01	3.1 ± 0.0	2.9 ± 0.0	66	56
1	12	0.19 ± 0.01	2.9 ± 0.0	3.0 ± 0.1	61	74
2	12	0.19 ± 0.01	3.7 ± 0.0	3.5 ± 0.2	54	63
3	12	0.20 ± 0.01	3.8 ± 0.1	3.4 ± 0.1	78	70
4	11	0.39 ± 0.19	3.7 ± 0.0	3.6 ± 0.1	65	84
5	11	0.15 ± 0.01	4.5 ± 0.3	4.7 ± 0.1	100	73
6	11	0.19 ± 0.00	3.0 ± 0.1	3.9 ± 0.1	99	91
24	11	0.23 ± 0.03	4.2 ± 0.2	5.4 ± 0.1	100	100

APPENDIX III

COPY OF SOUTH AFRICAN PATENT No. 93/7419

CHROME REMOVAL FROM TANNERY SOLID WASTES

THIS INVENTION relates to a waste water process for the removal of chromium from chrome tanned leather. More particularly, the process relates to a waste water treatment process for the removal of chromium, and the disposal of chrome tanned leather treated by the process.

In the production of chrome tanned leather, eg. wet blue, partially finished leather, and finished leather, chromium salts are introduced into the hide fibre as part of the tanning process. They cross-link with the hide protein (collagen) to form leather which is resistant to microbial attack. Thereafter a number of stages may be carried out, eg. fat liquoring, dyeing, finishing, etc. As a result the final leather or intermediate products, (such as the product known as wet blue leather) contain substantial amounts of bound chromium. When wet blue leather trimmings, shavings off-cuts, etc., are disposed of as a waste material, this causes problems due to its bulkiness in transport and requirement for specialised landfill disposal due to the chromium content.

Processes exist for removing chromium salts from various forms of chrome tanned leather by treating with lime, enzymes, etc. Hydrolysis of the leather takes place to give trivalent chromium ions in the form of a soluble precipitate, as well as sometimes a by product such as collagen. Such treatment of chrome tanned leather involves additional costs, including the cost of materials and fresh water added for treatment of the leather.

We have now found that a common waste liquor in the leather tanning industry can be used for treating chrome tanned leather to remove chromium ions therefrom and also to reduce the mass of solids, thereby involving a saving in recovery cost and making use of another potentially pollutive waste liquor.

The present invention provides a method of recovering chromium ions from hides and skins which have been processed with chromium ions to produce leather, or from leather in the form of processed goods which contain chromium ions, said process comprising digesting the leather with an alkaline effluent which contains sulphides at a temperature in the range of 70 to 100°C. Conveniently the pH of the effluent is greater than pH 8.5.

The chromium-containing leather to be treated in the process of the invention can be in a variety of forms. It can for example be a final leather product, finished leather or the intermediate known commonly as wet blue. Wet blue leather, in particular, is a bulky product, particularly when present in the form of shavings and trimmings. Shavings may be used directly in the method of the invention, whereas leather pieces conveniently may be shredded prior to treatment.

The effluent used for the treatment is an exhaust liquor from the treating process which contains significant quantities of sulphides and is very alkaline. The alkali present may, for example, be lime (calcium hydroxide) and/or an alkali metal hydroxide or carbonate, eg. sodium hydroxide or sodium carbonate. Analysis of effluent liquors available will indicate whether or not the liquor meets the requirements for treating (i.e. dechroming). A particularly suitable liquor is that known commonly as "dehairing or unhairing liquor" and is the effluent obtained from the dehairing of hides. This is an alkaline liquor of pH 10 to 13, (usually pH 12 or slightly higher) containing sulphide ions and a high organic content. Normally there are problems in disposing of this liquor because of its high organic content, alkalinity and smell. For example it usually has to be treated before combining with other waste streams by removing fat and grease, settleable solids and sulphides. The latter cause odour problems. With the present invention, this liquor after primary settling can be piped to a treatment facility for dechroming leather waste.

The treatment conveniently may be carried out in a temperature range of about 80 to 90°C with steam. We have found that after one hour a substantial amount of the chromium ions can be removed. The process may be continued for longer periods depending on the amount of chromium ions to be removed, the protein present, the strength of the unhairing liquor and the amounts of solids reduction required. Time periods of up to six hours have been utilised in testing the invention.

The treatment may be carried out in a container, which may be either open or closed apart from having an exit for excess steam (and therefore heat). As the process proceeds, there is a substantial reduction in the volume of the solids (protein) component which becomes soluble, leaving a small residue of solids, including a chromium precipitate. The bulk of the organic protein in the leather appears to be solubilised and is decanted with the waste liquor stream, free of chrome, discharged from the container. This waste liquor stream is passed to a conventional waste water treatment system as it is substantially free of contamination by chromium ions. The chromium ions can be removed with the small volume of precipitated solids after the dechroming process. If desired, this solid material may optionally be treated with acid, eg. sulphuric acid to produce a chromium sulphate solution and leave a substantially chromium-free solid waste for disposal to a non-toxic landfill or incorporated in a composting process. The chromium sulphate solution may be passed back to a pickling or other stage in the production of leather. This may lead to savings in the overall cost of leather production. The process provides a method whereby chromium may be retained in a closed cycle within the production process and hence reduce the environmental impact of the tanning operation.

Accordingly, the invention also provides a method of treating leather, which comprises the steps of applying chromium ions to hides and skins during a chrome tanning stage, thereafter, in a subsequent step removing the chromium ions from waste parts of the leather produced using the process of the invention; followed by extracting the chromium ions from the solid waste material, recovering the chromium ions as a soluble chromium salt, eg. the sulphate; and reusing the chromium salt in a tanning process. The chromium salts reused in the tanning process may be $\text{Cr}_2(\text{SO}_4)_3$.

Mass reductions of greater than 60% in the waste material (tanned leather waste, wet blue trimmings and shavings, or the like), and volume reductions of greater than 95% can be obtained with the process of the invention.

The invention is illustrated in non-limiting manner by reference to the accompanying drawing which shows a schematic way of carrying out the invention and worked Example.

In the accompanying drawing, a lime-sulphide-containing unhairing liquor of about pH 12 is introduced along line 10 into a primary settling tank 12. Supernatant overflows along line 14 into an open tank 16 which may be heated by steam or other suitable manner, eg. electrically. Chrome shavings, shredded off-cuts, waste leather and the like is introduced along 18 into the open tank 16 and heated to a temperature of 80 to 90°C.

Chrome-free exhaust liquor containing solubilised protein passes along line 20 to a waste water treatment plant 22. Solid precipitated material containing chromium passes along line 24 via dewatering and drying at 25 to a tank 26 containing acid. Acid is introduced into the tank 26 along line 28.

Chromium sulphate passes along 30 to a storage tank 32 for future reuse in pickling, tanning etc. A substantially chrome-free precipitate is removed at 34 for disposal as landfill.

Example:

100 kg chrome shavings (0.75m³ unpressed) were added to 2.55m³ lime liquor, giving a ratio of approximately 3:1 vol:vol.

Chrome shavings analysis: Dry solids = 50%
 Chrome in dry solids as Cr = 2%

Lime liquor - typical analysis:

pH	12.23
Conductivity	4 980mS.m ⁻¹
Sulphide as Na ₂ S	1 898mg.L ⁻¹
COD	9 744mg.L ⁻¹
Permanganate value	2 555mg.L ⁻¹

The mixture was heated to 80°C with live steam in an open vessel, agitated and held at this temperature for 2 hours.

- (a) Particle size was measured with a 4mm² sieve. Chrome shaving solids larger than this size were reduced to 5.8% of starting mass after treatment.
- (b) Sludge solids settled rapidly allowing a 95.5% recovery of the total sludge by sedimentation within 1 hour.
- (c) Settled sludge accounted for 22% of total treated liquor volume representing an approximate 100% reduction in solids volume at this stage.
- (d) Sludge could be recovered by decanting the supernatant solution and dewatering to approximately 50% solids dry weight. This represents a 60-70% reduction in the weight of the leather shavings requiring disposal and a 95% reduction in volume.
- (e) The supernatant was found to be chrome free and may be safely passed to a conventional biological treatment process.

- (f) The dried sludge was washed with 1M sulphuric acid with effected a 99.9% recovery of chrome in the acid fraction.

The resulting solids, being essentially chrome free may be either neutralised, passed directly to a composting process or disposed to non-toxic landfill.

- (g) The chrome laden sulphuric acid was used to make-up pickling tanning solution and a post tanning evaluation of leather produced using this source of pickle showed quality comparable to controls.

DATED THIS 6TH DAY OF OCTOBER 1992.

D.F. SHEPPARD
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APPLICANTS PATENT ATTORNEYS

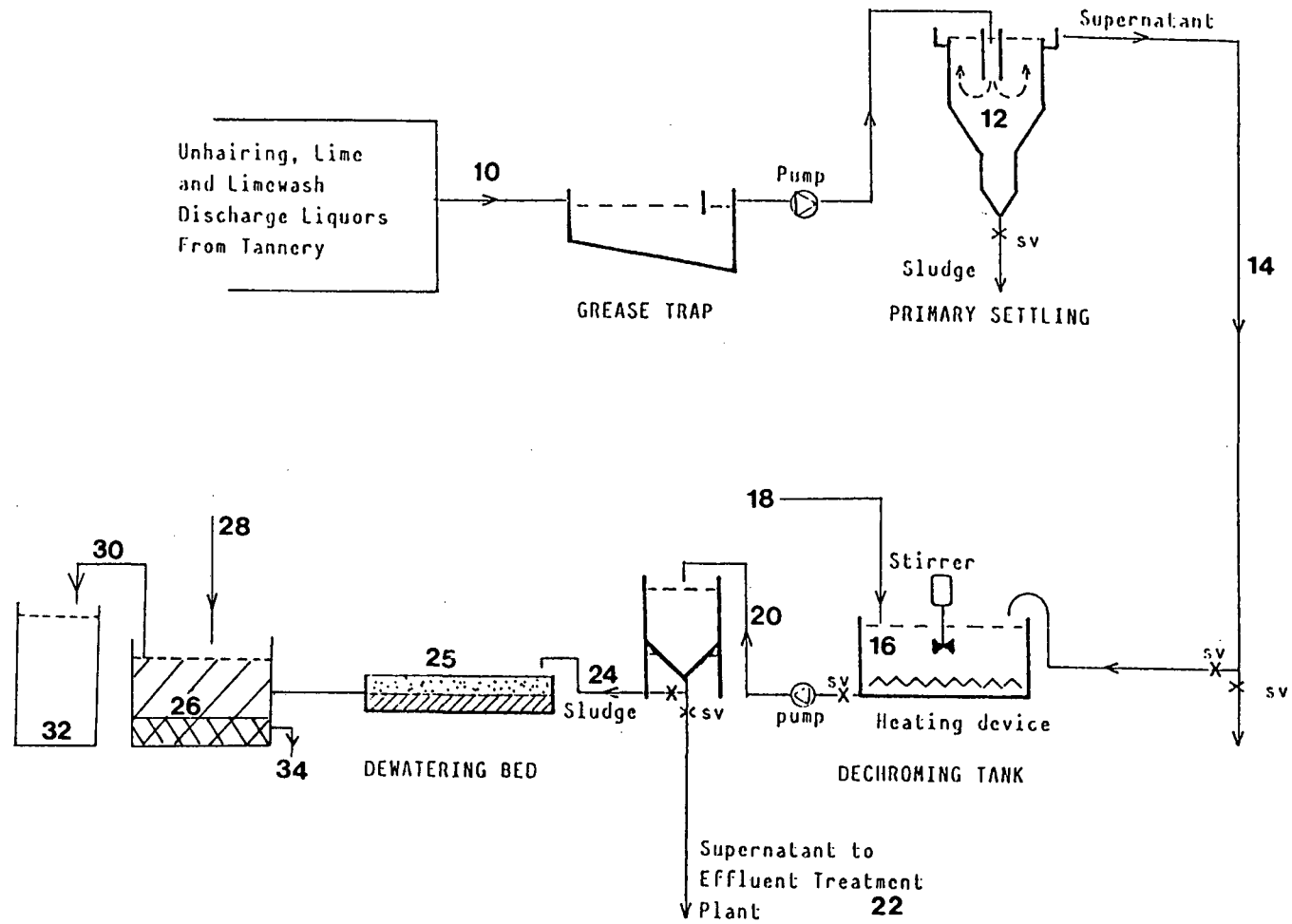


Figure 1: Diagrammatic representation of a system for dechroming tannery solid waste (shavings and trimmings).