Eco-benign Management Options for Cleaner Chrome Tanning

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Environmental regulatory laws have enforced the global leather industry to seek constant innovations in cleaner production. The pollution load on the environment due to increased chrome tanning activity has received much attention in India. It is recognised that one of the convincing solutions to the problems of sustenance of chrome tanning rests in the reduction of discharge of chrome in the effluent through in-plant control measures and cleaner tanning practices. Better management on the extent of discharge of chromium and compliance to discharge norms are the need of the hour. Here, an attempt has been made to focus issues relating to chrome tanning in India and discuss the technological means to achieve better management of chrome tanning in India.

Introduction

Leather industry has bestowed economic benefits in many of the developing countries on the one hand, whereas it suffers from the negative consequences of environmental impact of the tannery waste on the other. Among the various streams of tannery causing pollution, chrome tanning waste has attained much attention. The need to manage chromium better in global leather industry is widely recognised. Generally, chromium(III) salts are employed in tanning and this methodology is widely practised. The currently used basic chromium sulphate (BCS) salts and methods generally afford an uptake of 50-70 per cent of chrome used for tanning. This is attributed to high kinetic lability and poor thermodynamic affinity of some of the species contained in BCS salts.

In India, more than 90 per cent of hides and skin, processed annually, receive chromium in one form or the other. The annual use of BCS salts has been estimated at 50000 tonnes (ref.7). Although there is no authentic Assessment, based on the average exhaustion levels observed in the leather industry in the country, it is now likely that the economic value of this loss is nearly Rs 400 m/year (ref.8). The untreated effluents emanating from the chrome tanning sectional waste are found to contain 1500-3000 ppm of Cr(III). The discharge of chromium containing tannery wastes is of great environmental concern because of the biotoxicity of certain Cr(III) salts. The stipulated upper limit for the discharge of chromium in wastewater streams is 2 ppm in India. In order to meet the challenges arising out of this situation, concerted efforts through better surveillance of chromium with both in-plant and end-of-pipe treatment technologies have become imperative for the sustenance of the leather industry.

Several end-of-pipe treatment methods for tannery wastes have been explored and some have been adopted commercially, but these result in large quantities of chrome bearing sludge being generated, which are declared as hazardous wastes. Apart from this, the presence of sulphates in chrome tanning wastes lowers the efficiency of anaerobic lagoon. Therefore, a need for control of pollution through in-plant measures is evident. The in-plant control methods generally aim at saving of water and material, thereby reducing the pollution load.

It is recognised that one of the convincing solutions to the problems in chrome management rests in the reduction of discharge of chrome in the effluent through in-plant control measures and cleaner chrome tanning practices. Some of the technological means for the better management of chromium include:

- Chrome recycling methods.
- Chrome recovery/reuse methods.
- High exhaust chrome tanning methods.
- Less chrome technologies.
- Chromeless technologies.
- Avoiding chromium(VI) formation.
- Utilization of chrome shavings.
- Utilization of chrome sludge.

In this work, a comprehensive approach to the better management of chromium in tanneries is presented.

**Chrome Recycling Methods**

Spent-tanning solutions from a chrome-tanning yard can be recycled if the liquor is segregated and chromium is reused in successive tanning baths. There are two fundamentally different methods of reusing the unused chrome remaining after tanning. Chromium can be reused by either recycling the spent solutions directly or after recovering the unused chromium as chromic hydroxide and regenerating as basic chromium sulphate for reuse.19-26

Direct recycling of spent tanning solution from conventionally employed chrome tanning salts and methods have involved the use of spent tanning solution as a tanning or pickling bath for the subsequent batches. Spent chrome liquors are reported to contain, in addition to 0.25-0.50 per cent chromium, about 3.3-3.5 NaCl, 2.8-3.3 per cent of Na₂SO₄ (ref.5,23). Various reports are available on the direct recycling of spent chrome solutions.18,19,22-26

When spent chrome liquors were replenished with fresh chrome and reused for tanning the per centage uptake of chromium did not increase. This has been attributed to: (a) The structure and reactivity of the poor affinity species remaining unaltered during recycling and (b) Adverse influence of accumulated neutral salts on transport and uptake of the metal ion by skin. Various systematic studies have established that the utilization of chromium was not necessarily improved when the amount of chromium expelled from the leather during the mechanical operations, such as summery and setting are also taken into account. A continuous process of tanning, using an automated system in which the tanning alone is done at high pressure and spent chrome tanning solutions recycled has been reported. A two- stage tanning system has been reported to overcome the environmental problems of chrome tanning. This system affords direct reuse of spent tan liquor in the place of chrome-tanning salt for the subsequent batch in the first stage and efficient management of chromium present in the second stage by process linkage to the earlier operation. The process involves treatment of pickled pelts with 10 per cent chrome-tanning salt initially with sufficient quantity of water. After ensuring complete penetration of chromium in the pelt the bath is drained and collected for reuse. The chromium pre-treated pelts are subjected to basification subsequently.

For direct recycling of chrome in the chrome tanning stage the concentration of salt in spent tanning solutions need to be reduced below 1 per cent from a total of 7 per cent. Such reductions are not economically feasible. In view of the presence of large amounts of neutral salts the reuse of spent chrome solutions in pickling rather than chrome tanning appears an attractive alternative. One of the potential dangers in the direct recycling of spent chrome liquor of high chrome concentrations in pickle bath without proper pre-equilibration has been the harsh grain structure of resulting Leaths. Reuse of spent tanning solution in pickling also offers the advantage of containing salt pollution from tanneries.

A membrane-based technique for the selective separation of neutral salts from chromium through electrodialysis has been developed. The system couples the advantage of separation of the neutral salts contained in spent tanning solution from chromium and the use of neutral salt rich stream in pickling and chromium rich stream in tanning. The relative usefulness of electrodialysis concentrate stream as pickle and dilute as chrome tanning baths has been demonstrated. A closed loop based on electrodialysis is shown in Figure 1, to recharge the ground water from salt stream has also been examined. Since the application of such high technology inputs in recycling of chromium in tanneries is not yet established, recovery-reuse technique is gaining much more importance in the management of chromium in tanneries.

**Chrome Recovery/Reuse Methods**

The chrome recovery/reuse method involves the indirect reuse of spent chrome liquor. There is a potential to precipitate chromium from spent tanning solutions (using any alkali NaOH, Na₂CO₃, Ca(OH)₂, or MgO) as chromic hydroxide which can be converted to basic chromium sulphate by redissolution in sulphuric acid and reused.
This approach has found commercial acceptance in many countries including India. Although in principle, several alkalies can be employed, MgO is the preferred alkali in commercial practice. The relatively shorter settling time and favorable bulk density of the chrome hydroxide obtained have made MgO as the preferred alkali over others. The reactions involved in this method are given below:

\[
\text{Cr(OH)SO}_4 + \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Cr(OH)}_3 + \text{MgSO}_4 \quad \ldots (1)
\]

\[
\text{Cr(OH)}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Cr(OH)SO}_4 + \text{H}_2\text{O} \quad \ldots (2)
\]

\[
\text{MgO} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O} \quad \ldots (3)
\]

The settling of chrome hydroxide particles in suspension is governed by Stroke's law and influenced by: (a) Viscosity of the medium, (b) Difference of the densities of particulate matter and solvent media, (c) Temperature, (d) Stirring rate, (e) Dielectric constant, and (f) Size and shape of the settling particles. The zeta potential of the chrome hydroxide particles is expected to influence the nucleation properties as well as the ultimate particle size and bulk density of the chrome hydroxide. The electrolytes in the aqueous medium could also influence the electrokinetic phenomena and thereby the settling properties of the particles. It is, therefore, expected that by adjustments in the process control parameters, favourable settling rates can be realised.

The recovered chrome is reused as tanning salt in admixture with required fresh BCS salt after replenishment. The chrome recovery plants have already been commercially established in various parts of India and South Asia. A typical flow diagram for a commercial scale batch process is shown in Figure 2. The chrome recovery process lends itself to easy adoption in decentralised production base. This process is particularly useful for the wet blue tanners selling the wet blue stock to other finished leather manufacturers. This technology provides a convincing solution to the problem of chrome discharge into wastewater and in avoiding chromium in the sludge produced in composite tannery wastewater treatment. Since the process ensures that the sectional wastewaters from chrome tanning operation is segregated and handled, sulphate-bearing streams can be diverted away from the biomethanation reactors. This would facilitate a greater efficiency of biomethanation. The supernatant solution that comes out of the settling tank could be advantageously used for washing, soaking and pickling.

The salient features of the chrome recovery/reuse methodology are: (a) Complete recovery of chromium, (b) Simple and easy adoptability, (c) Commercially acceptance, (d) Ensures discharge of effluents satisfying norms for chromium, (e) Financially attractive with pay back period of one year, (f) leathers of acceptable quality, and (g) Suitability for small, medium, and large-scale units. Typical investments needed for the batch process for the settling of chrome hydroxide particles in suspension is governed by Stroke's law and influenced by: (a) Viscosity of the medium, (b) Difference of the densities of particulate matter and solvent media, (c) Temperature, (d) Stirring rate, (e) Dielectric constant, and (f) Size and shape of the settling particles. The zeta potential of the chrome hydroxide particles is expected to influence the nucleation properties as well as the ultimate particle size and bulk density of the chrome hydroxide. The electrolytes in the aqueous medium could also influence the electrokinetic phenomena and thereby the settling properties of the particles. It is, therefore, expected that by adjustments in the process control parameters, favourable settling rates can be realised.

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<table>
<thead>
<tr>
<th>Processing capacity (tonnes of hide/skins/yr)</th>
<th>Capital cost (Rs in lakhs)</th>
<th>Pay back period (yr)</th>
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</thead>
<tbody>
<tr>
<td>1.0 - 1.6</td>
<td>3.5</td>
<td>5.0 - 7.0</td>
</tr>
<tr>
<td>1.6 - 2.0</td>
<td>4.0</td>
<td>3.5 - 4.0</td>
</tr>
<tr>
<td>2.0 - 3.0</td>
<td>4.5</td>
<td>About 3.0</td>
</tr>
<tr>
<td>3.0 - 5.0</td>
<td>6.0</td>
<td>About 2.0</td>
</tr>
<tr>
<td>5.0 - 7.0</td>
<td>7.0</td>
<td>&lt; 1.5</td>
</tr>
<tr>
<td>8.0 - 10.0</td>
<td>8.0</td>
<td>&lt; 1.0</td>
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varying capacities as well as the pay back periods on the investments are given in Table 1. It is noticed from Table 1 that the pay back period of 12-18 months for the reactor capacities of 5-10 m³ makes the technology commercially sound from the tanner’s point of view. It has also been well established that the quality of the leathers obtained using this technology are very much comparable with that of normal BCS tanned leathers.

Currently, chrome recovery processes make use of batch type systems for the generation of chromic hydroxide. The process involves the addition of magnesium oxide to chrome bearing streams, allowing the chromic hydroxide precipitate to settle under gravity, followed by decantation of supernatant liquid. Magnesium oxide being a sparingly soluble alkali (0.00062 g/100 mL water) releases hydroxyl groups slowly. This results in longer duration for raising the pH to desired levels of 8.0-9.0. Further, because of poor solubility there is a tendency to add more amounts of alkali than required, resulting in the co-precipitation along with chromic hydroxide. Commercially available magnesium oxide contains large per centage of calcium salts, resulting in the generation of calcium sulphate, which also co-precipitates along with chromic hydroxide, making the reuse process difficult. The process of chromic hydroxide generation using MgO as precipitant alkali generates MgSO₄, which makes the ground water hard.

Alternatively, chrome recovery based on other alkalies like sodium hydroxide and sodium carbonate is gaining importance. When these alkalies are used the settling behaviour requires modification. The bulk density of the chromic hydroxide generated using sodium hydroxide and sodium bicarbonate is low and the bulk volume of the precipitate is larger. For efficient separation of the chromic hydroxide from the liquid media, other techniques like filter press or centrifugation may be necessary. In fact, technologies based on such removal methods are employed, especially when the volume involved is large. In other
words, there are many possibilities in the choice of chrome recovery/reuse technologies.

Considering the volume of leather processing activity in the country and the number of tanneries engaged in chrome tanning, more continuous chrome recovery modules, which would facilitate higher throughput of recovered chrome per working hour seems necessary. Further the increased popularity of high exhaust chrome tanning methods, tanning with low chrome offers and also common effluent treatment plants the magnesium oxide based batch systems may probably need reAssessments for higher volume activities of chrome tanning. Some of the most distinguished features between a batch type and continuous processes are given in Table 2.

Magnesium oxide may not be a suitable alkali for continuous chrome recovery due to its poor solubility, which results in nonachievement of the pH of 8.0-8.5 instantaneously. This calls for a change in the selection of alkali for continuous chrome recovery method. In order to replace MgO with other alkalis like sodium carbonate and sodium hydroxide, there is a need to improve the efficiency of the settling process. The settled volume of chromic hydroxide generated using sodium carbonate and sodium hydroxide under batch type chrome recovery system are 50 and 72 per cent as compared to MgO based system of 10 per cent. A commercial chrome recovery system, based on sodium hydroxide has been in practice. This method employs either filtration or centrifugation for achieving a thicker/denser cake. The other approach could be to improve the efficiency of settling for sodium carbonate and sodium hydroxide so as to avoid handling of more amount of chromic hydroxide slurry which leads to a dilute recovered solution. For this, particle-particle interaction and hence particulate characteristics needs to be improved. The size and shape of the settling vessel also influence the settling rate of the precipitate. A novel continuous chrome recovery system, based on sodium carbonate or sodium hydroxide that aids settling of chromic hydroxide through hydrostatic pressure built-up and turbulence has been designed and fabricated. The flow diagram of the semi-continuous chrome recovery system is shown in Figure 3. This semi-continuous chrome recovery system permits online separation of chromic hydroxide while maintaining a constant inflow to outflow ratio. The chromic hydroxide, formed earlier in a mixing tank, is allowed to flow under pressure through a pipeline where surface roughness and friction are enhanced. Then the suspension flows into an open well inside the settler, where the hydrostatic pressure and turbulence generated separate the chromic hydroxide from the supernatant.

High Exhaust Chrome Tanning Method

The uptake of chromium from tanning bath under normal conditions of tanning is of the order of 50-70 per cent of chrome used. The relatively poor uptake of chrome employed during tanning in the absence of any external-aid may arise from: (a) An intrinsic nature of the tanning salt, (b) The limitations of the functional sites needed in the protein for chrome uptake, and (c) The effect of environmental conditions employed before, during, as well as after chrome tanning. It is now possible to increase the absorption levels of chromium in the tanning through various strategies, which include: (a) Changing the conditions of tanning, (b) Use of exhaust aids, (c) Modifying basic chromium sulphate salts, and (d) Modifying protein substrate.

<table>
<thead>
<tr>
<th>Batch type</th>
<th>Continuous type</th>
</tr>
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<tbody>
<tr>
<td>- Batch size limitation of 10-12 m³</td>
<td>- Batch size limitation of &lt; 25 m³</td>
</tr>
<tr>
<td>- Recommended alkali - MgO</td>
<td>- Not limited by alkali choice</td>
</tr>
<tr>
<td>- Low investments</td>
<td>- Larger investments</td>
</tr>
<tr>
<td>- For chrome rich streams</td>
<td>- Wide range of chrome streams</td>
</tr>
<tr>
<td>- Adaptable to CETP's difficult</td>
<td>- Easy adaptability to CETPs</td>
</tr>
<tr>
<td>- Ratio of tank volume to effluent treated per day is 1:1</td>
<td>- Ratio of tank volume to effluent treated per day 1:3</td>
</tr>
<tr>
<td>- Economical for chrome rich streams</td>
<td>- Covers wider economic benefits</td>
</tr>
<tr>
<td>- Easy to adopt</td>
<td>- Calls for expertise and continuous monitoring</td>
</tr>
</tbody>
</table>
Tanning can be considered, in principle, to be a chemical reaction between a solid substrate and species contained in a condensed liquid phase. It is logical to expect the uptake of chromium(III) salts by protein to be influenced by those environmental factors which affect the interfacial processes in protein-chromium(III)-water interface. The factors, such as pH, temperature, float, basicity, masking, neutral salt concentration, drum geometry, and speed influence both diffusion and chemical equilibria implicated in tanning process. Systematic investigations have shown earlier the trends in chrome tanning efficiency as a function of process variables. There have been approaches to carry out tanning at relatively higher pH conditions such that chromium contained in unspent chrome liquor is modified and their deposition into skin structure increases. Several modifications of this approach including direct recycling of spent chrome tanning solution as pickle bath have been adopted and used in commercial practices.

The process of chrome tanning has evolved over the years and maximum level of exhaustion of chromium possible by the use of conventional chrome tanning salts and methods have already been optimized by variations in process parameters, involved in tanning.

It is now technically possible to improve the exhaustion levels of chromium through the use of external aids, which may: (a) Increase the substantivity of the protein matrix to chromium. (b) Promote the build up of poly nuclear complexes of chromium, and (c) Adsorb or chemisorb unspent chromium and deposit inside the protein matrix. Many chrome exhaust aids are already available in the market. Known external chrome exhaust aids are based on: (a) Polyhydroxy aluminium chloride gels, (b) Polymides, (c) Polycarboxylates, (d) Long chain alkanolamines, (e) Polyelectrolytes, (f) Protein hydrolysate, (g) Silicates of magnesium or aluminium, (h) Oxazolidines, (i) Heavy metal oxides, (j) Phosphates, and (k) Ion-exchange resins of suitable particle sizes. These exhaust aids may help in fixing more chromium by creating additional sites for the interaction of chromium. Exhaustion levels of the order of 85-95 per cent have been reached by making use of exhaust aids. There are also arguments that the maximum level of chrome absorption possible is about 95 per cent of the metal ion employed. The non-uniform distribution of
chromium under the action of external chrome exhaust-aids is, however, unlikely. In the event of nonuniform distribution of chromium the post-tanning operations will be affected\(^{49}\). In spite of several claims on the advantages in the use of external chrome exhaust-aids the commercial level of exploitation of such aids seems to be limited. New approaches are necessary, if substantial improvements in chrome uptake are to be achieved without resorting to the use of any external exhaust-aids.

A true scientific approach to increasing the exhaustion levels of basic chromium sulphate rests in: (a) Identifying the nature and molecular structures of major \(\text{Cr}^{(III)}\) species not being absorbed during tanning and then, (b) Evolving methods to avoid the formation of low affinity species through directed synthesis strategy for the manufacture of BCS. The benefits of this approach have already been demonstrated\(^{50}\).

The chrome tanning salt, basic chromium sulphate is invariably prepared by the reduction of chromium(VI) with various reducing agents under aqueous acidic conditions\(^{49,50}\) and basifying the resulting chromium(III) complexes to ensure an OH to chromium(III) ratio of 1:1. Several reaction process parameters, such as ratio of chromium(VI)/acid, reaction temperature, the order and rate of addition of reactants, pH at the time of completion of reaction, ageing time and basification pH may influence the ultimate composition and constitution of BCS salts\(^{50,51}\). Chromium(III) complexes of different molecular structure and reactivity are generally formed during the reduction of chromium(VI) depending on the reaction conditions. These are particularly relevant because the duration of tanning under commercial conditions is limited generally to a period of 4±1 h\(^{,17}\). It has been shown that there are more than 15 structurally different chromium(III) species in BCS salts, varying in degree of polymerisation charge, number of coordinated aqua ligands and the type of nonaqueous ligands coordinated to metal ion\(^{51,55}\). It is logical to expect that the chemical reactivities of these different species could be varied. If any particular species is to be taken up quantitatively by the skin protein collagen within 4-5 h, Asscuming an unlimited supply of functional sites in collagen, a pseudo first order rate constant exceeding \(2 \times 10^{-3} / s\) is necessary for aqua-ligand substitution in chromium(III) complexes. This is expected because the theories of chrome tanning postulate that the irreversible binding of chromium by the protein occurs due to coordinative interactions between carboxyl sites of collagen and chromium(III) ions. Whereas the kinetic considerations provide clues with respect to relative ease of interaction the irreversibility in binding of chromium may be achieved only if the binding is thermodynamically favourable and binding constants for Eq. (1) are greater than \(15 / M\).

\[
[(\text{H}_2\text{O})_6\text{Cr(OH)}_2\text{Cr(H}_2\text{O})_4]^{12+} + \text{P-\text{COO}}
\]

\[
[(\text{H}_2\text{O})_6(\text{P-\text{COO}})\text{Cr(OH)}_2\text{Cr(H}_2\text{O})_4]^{3+} + \text{H}_2\text{O},
\]

where \(\text{P} = \text{protein matrix}\).

Structure affinity relation studies with the various chromium species present in BCS have led to the identification of a tetrameric chromium species with a 4+ charge as the low affinity species\(^{53,54}\). BCS is found to contain about 15 per cent of the low affinity species and this species accounts for nearly 40 per cent of chromium in the effluent. Low affinity of this species to collagen has been traced to high kinetic lability and lower binding constant for its complexation with functional sites in collagen\(^6\). The amount of a low affinity tetrapositive tetrameric species present in BCS is known to influence the exhaustion behaviour of the tanning salt. Through designed alterations in the manufacture of basic chromium sulphate salt, a modified BCS salt exhibiting an exhaustion level of above 85 per cent of chromium offered, which is devoid of low affinity species has been reported\(^{5,56,72}\).

There have been reports, however, of attempts to augment chrome binding sites in the protein matrix and enhance chrome uptake. Increasing the number of metal binding sites in collagen can increase reactivity of the protein in chrome tanning\(^{51,56}\). The simplest method to increase the number of carboxyl sites in collagen is to subject the amide side chains of asparagine and glutamine to alkali hydrolysis as in the case of liming\(^7\). Another method of increasing the number of carboxyl groups is to condense active hydrogen compounds containing carboxyl groups with the side chain amino groups of collagen, using the Mannich Reaction or related condensates as well as grafting acrylic comonomers\(^{57,58,59}\). Another approach of increasing the chrome uptake is based on catalysing the reaction of inert chromium species present in the chrome liquor. A catalytic cycle mechanism has been proposed for improved
exhaustion of chrome by the use of monoethanolamine during tanning due to its ability to involve in hydrogen bonding with carboxyl groups. Monoethanolamine based chrome tanning system enables greater than 90 per cent exhaustion of chromium.

Chrome saver approach, involving a combination of chromium with other tanning agents like aluminium, zirconium, iron, silica, and titanium compounds or glutaraldehyde or its derivatives, has been found to be an effective approach to decrease the chrome content in spent tanning solutions. The added advantage of these systems, apart from reducing the amount of chromium in the spent tan liquor, is in imparting the desired physical and chemical properties.

It is now technologically possible to increase the absorption of chromium during tanning through various strategies such that the absorption exceeds 85 per cent of the chromium(III) employed. Such high exhaustion methods afford wastewater from sectional chrome tanning streams with chromium concentrations in the order of 300-750 ppm. However, the spent chrome liquor from such streams can be recycled directly as a pickle bath without impairing the quality of leathers. Under favourable conditions, Austrian tanneries have been able to employ such direct recycling methods. These streams are not directly amenable for discharge. While economic advantages of the high exhaustion chrome tanning are evident, further processing of waste streams of chrome tanning yard needs to be integrated. Although various methodologies are available, a popular chrome saver approach based on aluminium-chromium combination tanning, which has economic process viability as well as easy applicability, is presented here.

**Alutan-Chrome Combination Method**

Polyhydroxy aluminium gels are known to aid the exhaustion of chromium during tanning and function as a chrome saver. The reversibility of aluminium binding to Leath has, however, limited the utility of previously known processes based on Al(III) salts as chrome savers. High performance aluminium based tanning agent “Alutan” which is commercially available as Balsyn AL has aluminium in the stabilised form and is irreversibly bound to the substrate. The product is based on a polymeric network carrying suitable liganding sites to increase chrome fixation when used with BCS salt, thereby functioning effectively as a chrome exhaust aid as well as chrome saver.

A high exhaust chrome tanning method has been developed based on alutan-chrome combination involving the use of 1.5 per cent alutan and 5.0 per cent BCS salt (based on pelt weight). Exhaustion levels of above 90 per cent of chrome and aluminium are possible with this system and the resultant wet blue leathers possess the required hydrothermal stability. The chrome concentration in the spent tanning liquor obtained by this method is normally in the range of about 500 ppm. This limit does not permit direct discharge of the waste solution without further treatment. At this chrome concentration the chrome recovery method may be less economical as compared to normal chrome tanning. Other alternative, i.e., chrome management methodology, which provides saving of water, chemicals and reduction of chemicals is recycling of waste chrome solution as pickle float or tan float. Although, direct recycling of spent chrome liquor of high chrome concentrations (> 1000 ppm) in pickle bath without proper pre-equilibration is known to cause grain coarseness, the spent chrome solution of high exhaust chrome tanning method can be advantageously recycled without any danger. Therefore, a combination of high exhaustion chrome tanning with recycling of the spent tanning solution as pickle bath in the successive batches seems to be realistic.

**Closed Loop Alutan-BCS Combination System**

High exhaustion methods ensuring an absorption of about 90 per cent of the salts may not be environmentally acceptable without forward linkages to reuse methods for the remaining 10 per cent of chrome in sectional streams. Such methods have now emerged. Typical method, based on the use of aluminum syntan in combination with chrome is shown in Figure 4. It is known that BCS contains 30-35 per cent of neutral salts in the form of sodium sulphate. Further the basification process in chrome tanning also leads to the formation of sodium sulphate. Hence the spent chrome tanning solution contains about 2.8-3.3 per cent of sodium sulphate. Recycling of spent chrome liquor involves accumulation of sulphate from the BCS salt as well as the neutralised acid. To maintain the same salt content in the pickling for the recycling experiments, pickling with sodium sulphate is considered.
Figure 4 - Closed loop minimum waste chrome tanning

Pickling system has the additional benefit of easier treatability of waste streams with respect to neutral salts. Sodium sulphate (5.0 per cent on pelt weight) pickling to a pH of 2.8-3.0 was carried out. To the same pickle float, BCS was added and tanning completed. After the completion of chrome tanning, the spent chrome liquor was collected, filtered, and reused as a pickle float for the next batch. No addition of salt is required. Recycling of spent chrome liquor can be repeated continuously, thereby no liquor is discharged. The results of the spent liquor analysis and shrinkage temperature measurements of the wet blue leathers for three recycles are given in Table 3. The physical and chemical analysis data shows that these leathers meet the required specifications. This technology is being implemented commercially in many tanneries at Kanpur, Jallandhar, and Dindigul.

The cost-effectiveness of the alutan-BCS method has been established in commercial scale tanneries. The exhaustion levels of chromium and aluminium exceeding 90 per cent have been obtained. The potential benefits of the process, as observed in a commercial scale production in tanneries are as follows:

- Promises near total utilization of chromium.
- Promises water saving from pickling and tanning operations by about 90 per cent.
- Promises material economy.
- Permits reduction in wet finishing chemicals, wattle: 30-40 per cent, retanning agents: 20-30 per cent, and dyes: 10-20 per cent.
Table 3 — Per cent exhaustion and shrinkage data of closed loop system

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Per cent exhaustion</th>
<th>T (°C)</th>
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<tbody>
<tr>
<td>Chromium</td>
<td>75</td>
<td>118</td>
</tr>
<tr>
<td>Aluminium</td>
<td>95</td>
<td>118</td>
</tr>
<tr>
<td>Pickling</td>
<td>97</td>
<td>116</td>
</tr>
<tr>
<td>Tanning</td>
<td>96</td>
<td>114</td>
</tr>
<tr>
<td>Recycle 2</td>
<td>92</td>
<td>116</td>
</tr>
<tr>
<td>Recycle 3</td>
<td>92</td>
<td>116</td>
</tr>
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</table>

- Promises reduction of BOD, COD and TDS load by 90 per cent from the identified streams on the ETPs.
- Promises an overall savings in the manufacturing cost of Rs1200-2000/t of raw hides and skins processed.
- Affords fuller leathers in comparison to normal chrome tanned leathers.
- Affords leathers of desired physical and chemical properties.

A typical cost flow sheet for the vertical linkages with crust leather production is given in Table 4 where the conventional and closed loop processes are compared. This method eliminates the use of high amounts of neutral salts and the direct benefits from the process include reduction in dissolved solids. This process is cost-effective for the tanneries, which are vertically linked in the conversion of raw hides or skins into dyed crust or finished leather. For the wet blue tanneries, this process may not be attractive until the market is able to bear the extra cost of tanning and share the cost benefits through savings in chemicals at the retanning and dyeing stages. The increase of 10 per cent in the cost of tanning can be offset by just 2 per cent saving in the post tanning chemicals. This process promises a saving of nearly 20 per cent in the cost of retanning and dyeing.

Table 4 — Cost analysis of closed pickle tan loop

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<thead>
<tr>
<th>Operation</th>
<th>Normal process (Rs)</th>
<th>AlutJn-BCS (Rs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pickling</td>
<td>400</td>
<td>550</td>
</tr>
<tr>
<td>Tanning</td>
<td>2300</td>
<td>2500</td>
</tr>
<tr>
<td>Post tanning</td>
<td>7000</td>
<td>5400</td>
</tr>
<tr>
<td>Total cost</td>
<td>9700</td>
<td>8450</td>
</tr>
<tr>
<td>Overall savings</td>
<td>1250</td>
<td>1700</td>
</tr>
</tbody>
</table>

Less Chrome Technologies

Alternative mineral tanning agents form an easy means for better management of chromium in tanneries, but the molecular events involved in tanning with a particular salt or material are not easily reproduced by alternatives. Although, combination of organic and mineral tanning it could be possible to match the shrinkage temperature of chrome-tanned leather as in the case of aluminium-mimosa method, it may not be possible to match the chemical character of the chrome tanned leather with respect to the versatility and molecular stability using alternative methods of tanning. In order to have the benefits of chromium as a prime tanning agent to achieve the required properties on one hand and pollution control on the other, less chrome technologies based on reduced amounts of chromium in combination with alternatives are gaining importance. As a chrome saver approach, a chromium-iron tanning agent has been developed. In a selected ligand environment the negative attributes of iron tanning such as deterioration and darkening of colour on ageing were avoided. The leathers processed thereby meet all the required chemical and physical properties. Natural colours based on Cr-Fe tanned leather by treating with various vegetable tanning materials have been developed. A novel chrome-silica tanning agent developed provides better bulk properties to the leather namely softness, smoothness, fluffiness, fullness, apart from increased chrome exhaustion. With increased demand for formaldehyde free syntans, products based on formaldehyde-free chrome and aluminium have been developed. An additional advantage is avoidance of pickling, thereby reducing the pollution load from pickling operation.

Chromeless Technologies

There has been an ongoing search for alternatives to chromium as a tanning material. Primary motivation for such a search has been due to
environmental concerns associated with the discharge of unused chromium and the potential problems in the safe disposal of solid wastes containing the metal ion. Life cycle analysis of chrome tanned leather has not yet been carried out scientifically; but there is sufficient ground to raise questions against the disposal of used chrome tanned leathers through incineration. Since chromium is not a renewable resource, alternative systems are necessary for industrial applications; especially if the metal ion plays a critical role in tanning industry.

The use of alternative mineral tanning salts, based on aluminium, titanium, zirconium, iron, zinc, and silica has been proposed and attempted with varying degrees of success. Total replacement of chromium by other mineral tanning salts has been attempted without much commercial impact. The newly developed zirconium based tanning salt helps to overcome the known disadvantage of basic zirconium sulphate salts, viz. drawn grain of resulting leathers and the need to employ acidic pH (< 2.5) for tanning. Any serious changes in tanning would call for significant alterations in both beam house and post-tanning operations. A phenomenological approach has been adopted to locate alternatives to chromium as a tanning material.

**Chromium(VI) Formation in Leather — A Cause for Concern**

The formation of chromium(VI) in the final leather has become a serious problem in the context of ecobenign leathers. The entry of chromium(VI) into leather could be through some undesirable redox reaction between Cr(III) based tanning salt and oxidizing compound. The formation of hexavalent chromium from trivalent chromium may be due to three main reasons, namely (i) Oxidation by air, favoured by high pH, (ii) Photo-ageing - oxidation by air when the leather is subjected to light, and (iii) Thermal-ageing - oxidation by air when the leather is subjected to heat. The formation of chromium(VI) in leather could be avoided by double spear prone attack. First, by avoiding the usage of chemicals like ammonia used in dyeing, fish oil based fatliquors and post-tanning finishing chemicals with uncontrolled oxidative catalyst, which aid the formation of Cr(VI) and secondly by approach involves usage of reductants, like sodium bisulphite and sodium thiosulphate under proper conditions.

**Utilization of Chrome Shavings**

Better management of chromium in tanneries would be complete only with application of technologies for utilisation of chrome shavings and buffing dust as well as safe disposal of chrome tanned leather based products. It is believed that for economic reasons, better utilisation of solid wastes would become a standard industrial practice within the next 10 y. A holistic solution to the technological problems faced by the leather sector is feasible. Such a solution would involve also the safe recovery of chromium from used leather products.

Leather processing is one such industrial activity, which generates chromium-bearing wastes in different forms. One of them is chrome shavings and this contributes to an extent of 10 per cent of the quantum of raw skins/hides processed, amounting to 0.8 m t globally. Although several methods for the utilization of chrome shavings have been reported earlier, but the presence of chromium posed problems. Recent study on chrome shavings from leather processing has indicated the usefulness of chrome shavings as a potential reductant in the preparation of basic chromium sulphate, which can be advantageously used for tanning. This route provides a safe means for the disposal of chrome shavings. The developed product exhibits more masking due to the formation of intermediate organic oligo-peptides. The formation of these organic masking agents helps in chrome tanning by shifting the precipitation point of chromium.

**Utilisation of Chrome Sludge**

Regardless of the application of the cleaner processing method adopted the composite wastewater would contain some residual chromium as a result of washings. The chromium sludge from physico-chemical treatments could be utilised without the danger of chromium being leached. This has now been achieved through a technology for the production of bricks from a mixture of clay and sludge in 85:15 per cent composition. This offers a true and viable solution to the problem of chrome sludge discharge. Since the organic matter in chrome sludge could be used as internal fuel, it is possible to reduce the costs of brick production. Another attractive proposition for removing chromium from spent chrome liquor is by bioaccumulation. Although some reports do suggest the possible use of microorganisms, such as bacteria and fungi in the
removal of chromium(III) salts from spent chrome solutions. A commercially acceptable bioaccumulation process is yet to be developed.

Conclusions

Although there have been predictions that chromium would be replaced in tanning by other materials, it is our opinion that total replacement of chromium in tanning may not be realistic or required within the next 20 y. Better management of chromium will be the immediate direction of choice in tanneries.

A feasible solution to the survival of chrome tanning includes the adoption of either chrome recovery/reuse process (for wet blue manufacturers) or closed pickling loop with high exhaustion chrome tanning for an integrated (raw to finish type) tannery. The discharge of chromium and dissolved solids in wastewater can be contained through process-product changes employing organic or less-chrome or chrome-less technologies. The formation of chromium(VI) in the leather can be avoided through proper process control measures. Therefore, in-plant control appears the most attractive solution to chrome tanning related pollution problems. Apart from these methods, viable approaches for chrome shavings and chrome sludge utilization have also been highlighted.

References

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