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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION

REGIONAL PROGRAMME FOR POLLUTION CONTROL IN THE TANNING INDUSTRY IN SOUTH EAST ASIA

TECHNOLOGY PACKAGE

A SYSTEM FOR RECOVERY AND REUSE OF CHROMIUM FROM SPENT TANNING LIQUOR USING MAGNESIUM OXIDE AND SULPHURIC ACID

TECHPACK/UNIDO/RePO/1

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ABBREVIATIONS USED

approx Approximately

BCS Basic Chromium Sulphate

BS British Standards

BIS Bureau of Indian Standards

CLRI Central Leather Research Institute

cm Centimeter

Cr Chromium

FRP Fibre Reinforced Plastic

H₂SO₄ Sulphuric Acid

HDPE High Density Polyethylene

IP Insulation & Protection

IUP International Union Physical

KVA Kilo Volt Ampere

m Meter

MgO Magnesium Oxide

mm Millimeter

PP Polypropylene

PVC Poly Vinyl Chloride

rpm Rotation per minute

Sq. Square

SS Stainless Steel

UNIDO United Nations Industrial Development Organisation

$\boxed{1}$

OBJECTIVE

1.1 PREVALENT PRACTICES

In traditional chrome tanning it has been observed that generally 60 - 70 % chromium applied in the form of basic chromium sulphate (BCS) is absorbed by the hides and skins under process and the balance is discharged as waste in the effluent.

1.2 GENERAL CONSIDERATIONS

The chromium discharged as waste signifies a big loss as well as an environmental hazard. For example, the tanneries in India currently discharge a large quantity of chromium salt, estimated at 17,000 tons per year, as waste. The presence of chromium in tannery effluent causes environmental pollution. High concentration of chromium in the effluent complicates its treatment, besides increasing the cost of treatment. Disposal of chromium containing sludge costs more as, in many countries, such sludge is regarded as hazardous.

1.3 NEED FOR TACKLING THE ISSUE

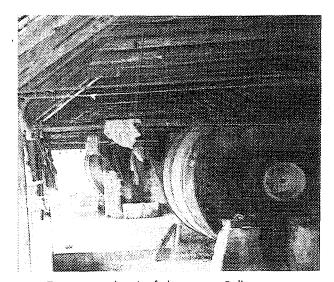
The chromium concentration in terms of total chromium (Cr) in the exhaust chrome liquor ranges from 1,500 – 5,000 mg/litre and the volume of exhaust chrome liquor is 4 to 6% of the total volume of wastewater discharged from the tanning process. This exhaust chrome liquor is generally mixed with other streams of effluent in a tannery and the concentration of chromium as Cr in the composite stream ranges from 100 – 300 mg/litre. In most countries, pollution control authorities insist that the treated effluent should contain less than 2 mg/litre of chromium as Cr.

1.4 EVOLUTION OF THE TECHNOLOGY

Indirect chrome recovery and reuse method involves segregation and collection of exhaust chrome liquor, precipitation of chromium with the help of an alkali, and regeneration of chromium using sulphuric acid for reuse in chrome tanning. All types of alkalies, such as sodium hydroxide, sodium carbonate, sodium bicarbonate, magnesium oxide, calcium sulphate, lime etc. have been considered in the indirect chrome recovery method. It has been found that magnesium oxide (MgO), because of its low reactivity and solubility, causes chromium to settle compactly. This makes the chromium separation from the exhaust liquor easy as it only involves decantation of the supernatant. Dissolving the recovered chromium can be done instantly with sufficient sulphuric acid to obtain reusable liquor.

1.5 FOR WHOM IS THE TECHNOLOGY RELEVANT

Chrome recovery systems with sophisticated mechanical units developed and adopted in large scale tanneries in industrialised countries cannot totally be replicated in the developing countries of the South East Asian region due to the small scale and traditional nature of the tanning process, limited technical manpower capabilities and other infrastructural bottlenecks. In such countries, the technology described in this package is quite relevant as it is easy to adopt, besides being cost effective.



Tanning yard in Arafath tannery, Pallavaram

1.6 OBJECTIVE OF THE TECHNOLOGY PACKAGE

The chrome recovery and re-use system using MgO as an alkali for chrome precipitation and sulphuric acid to regenerate chromium solution is simple and viable, both technically and commercially. A commercial scale chrome recovery and reuse system has been designed and implemented by Central Leather Research Institute (CLRI), Madras, India at M/s. Arafath leathers (a commercial tannery), Pallavaram near Madras under the UNIDO project of technical assistance in India (US/IND/90/244). This chrome recovery system has been in continuous operation from September, 1994. With a view to disseminate and promote the successful chrome recovery and reuse technology this comprehensive guide is compiled as a technology package by the Regional Programme Office of UNIDO at Madras under the guidance of Mr. Jakov Buljan, Senior Industrial Development Officer, ISED/AGRO, UNIDO, Vienna.

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PROCESS DESCRIPTION

Chrome management in a tannery may comprise any of the following methods and sometimes a combination of these.

2.1 HIGH CHROME EXHAUSTION

This process aims at increasing the rate of absorption of chromium in hides and skins under process to 85 - 90 % or more. For high chrome exhaustion better drums with high capacity driving system, strict process control of parameters like pH, temperature, etc. and additional special chemicals are needed. High chromium exhaustion would increase the cost at wet blue stage, but is likely to result in savings in chemicals at the finishing stage. However, high chromium exhaustion may not be feasible in most of the traditional tanneries with the existing drums and infrastructural facilities, particularly in tanneries processing raw hides and skins to wet blue stage only.

2.2 DIRECT RECYCLING OF SPENT CHROME LIQUOR

The direct reuse method envisages reuse of exhaust chrome liquor directly after simple screening as tanning liquor for the next batch. Additional chromium is supplied to compensate the deficiency. The main constraint in adopting this method is that the salts and other impurities are accumulated due to repeated reuse and will have negative effect on the leather quality. After a few recycles the exhaust chrome liquor has to be discharged as waste.

2.3 RECOVERY OF CHROMIUM AND ITS REUSE - INDIRECT REUSE METHOD

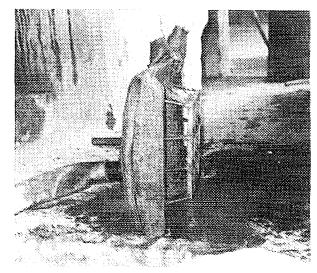
Under the indirect reuse method, chromium is recovered by precipitation as hydroxide using an alkali and the precipitated chrome slurry is dissolved subsequently in sulphuric acid. The solution can be used as tanning liquor. The advantage of this method is a more efficient use of chromium and a cleaner reusable solution which normally does not affect the leather quality.

2.4 SEPARATION OF CHROMIUM COMPOUNDS

In principle, by this method, recovery of chromium can be achieved by separating the chromium compounds from other salts in the waste liquor. The chrome liquor may be cleaner than by the direct reuse method, but this system requires rather sophisticated techniques such as electrodialysis, membrane separation, ion-exchange etc. and has limited scope for implementation in tanneries.

2.5 USE OF ALTERNATIVE CHEMICAL(S) FOR TANNING

Various alternative chemicals like aluminium and zirconium based salts have been tried in the tanning industry, but these have certain limitations vis-à-vis the quality of finished leather required. Accordingly these are applied on a limited scale only.



Special door with flexible hose pipe

Of all the options described above, the chrome recovery and reuse system using MgO as alkali has found much favour in India, particularly among the small tanners, as it can be used either for an individual tannery (if the quantum of spent chrome liquor discharged justifies it) or for a group of small tanneries (each bringing its spent chrome liquor once in 2 or 3 days to the recovery unit and taking back the recovered chromium for reuse). This technology package dwells on recovery of chrome and its reuse by indirect reuse method only.

In Figure 2.1, the process flowchart of recovery of chrome and regeneration for reuse may be seen. The spent chrome liquor from the tanning drum is discharged through a special door fixed with flexible hose pipe to the collection trap. The flexible hose pipe will be as long as required depending on the location of the collection trap. A screen chamber is provided at the end of collection drain before discharge into the collection tank. From the collection tank, the spent liquor is pumped into the main reactor. Before entering the main reactor, it is screened again.

In the main reactor the alkali, magnesium oxide (in solution form) is added slowly, when the stirrer is

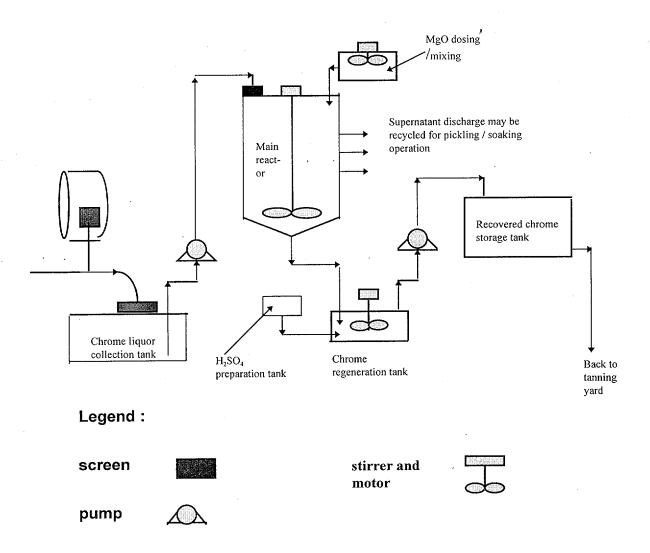


Figure 2.1 Flow Diagram of the chrome recovery and re-use process

operational. This process takes one hour. The stirrer is thereafter stopped and the precipitated chromium settles in the form of a compact slurry in the bottom in about 4 hours. Supernatant is discharged through side valves at different levels in the main reactor and the chrome slurry is discharged from the bottom by opening the bottom valve. The chrome slurry is redissolved and acidified in the chrome regeneration tank by adding sulphuric acid,

keeping the stirrer on. The recovered chrome after natural cooling for 3-4 hours is pumped from here to the recovered chrome storage tank. The recovered chromium in the form of solution is collected in buckets and used in normal chrome tanning operation, generally in the ratio 70 % market BCS to 30 % recovered chromium. The whole process can start afresh from here. The detailed drawings are given in Annexure III.

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MECHANICAL EQUIPMENT

3.1 INTRODUCTION

The mechanical equipment requirement for a chrome recovery system suitable for a medium sized chrome tannery processing 5 to 6 tons of raw hides and skins a day and discharging 6000 to 9000 litres of exhaust chrome liquor, both from main chrome tanning and rechroming operation, is given below. In case the capacity of the tannery is less than 5 tons per day, the dimensions of the reactor and storage tanks may be reduced proportionately. Similarly, the capacity of the pumpsets and stirrers may too be reduced (It is always advisable to be on the higher side with dimensions and capacities!).

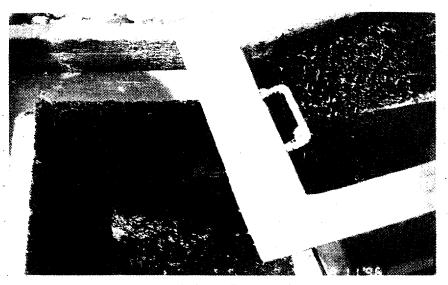
The list of equipment is as follows:

- Screens, on the collection drain of spent chrome liquor.
- Pump for chrome effluent transfer
- Main reactor and stirrer
- Magnesium oxide tank and stirrer
- ➡ Chrome regeneration tank and stirrer
- Sulphuric acid dosing tank and (optional) pump
- Pump for regenerated chrome liquor
- Recovered chrome liquor storage tank

These are described in the following paragraphs. The detailed equipment specifications for procurement are given in Annexure II.

3.2 SCREENS

The following types of screens are needed for removing suspended impurities from the exhaust chrome liquor. Stainless steel screen made of stainless steel bars for drum door, slightly smaller than door size (approx. 15%). A fire hydrant type valve in brass fixed in the middle of the screen. Flexible PVC hose pipe of sufficient length is fitted to discharge the chrome liquor through the collection trap provided in the drain leading to collection tank.



Screen before collection tank

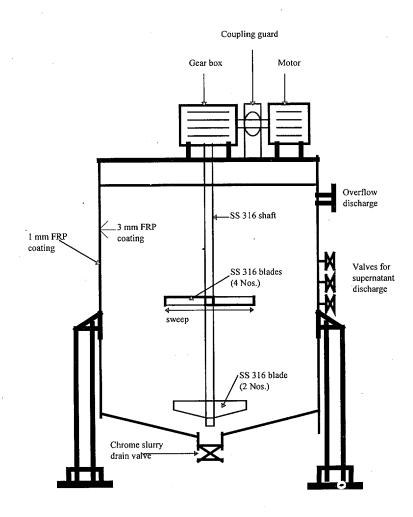


Figure 3.1 Main Reactor

Stainless steel screen with progressive perforated holes to be fixed at the inlet point of the spent chrome liquor collection tank. Dimensions have to suit the chrome effluent screening chamber. On top a stainless steel handle is fixed. On welded joints fibre reinforced plastic (FRP) must be coated.

Basket screen at the inlet of the main reactor. Its dimensions are generally $0.40 \times 0.40 \times 0.2$ m depth with a stainless steel mesh.

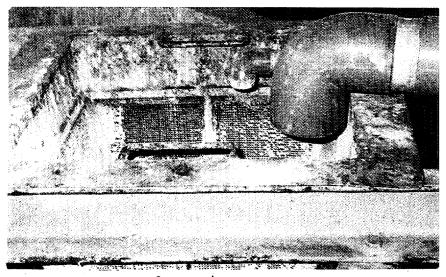
3.3 MAIN REACTOR

The main chrome precipitation reactor (Figure 3.1) of a capacity of 9 cubic meter (per batch) is made of flat sheet mild steel with fibre reinforced plastic (FRP) linings using bisphenol resin and epoxy inside and one layer FRP as surface mat outside.

The bottom slope is in the range of 5 - 15°. The reactor is supported by 4 columns in heavy duty mild steel of 2.2 to 2.8 meters height, fitted with base plate, fixers and cross angles. All connections, bolts and nuts are in stainless steel including the fixers of polypropylene anti-corrosive sluice ball valves (supernatant discharge) as well as a provision for overflow discharge. Cast iron special anti-corrosive valve for chrome slurry withdrawal is fitted at the bottom.

3.4 STIRRER FOR MAIN REACTOR

The shaft of the stirrer is in stainless steel for a length of about 3 meters with two sets of stainless steel blades, one in the middle (4 blades) and the other at the bottom (2 blades). The stirrer is driven by a motor coupled to a



Screen in the main reactor

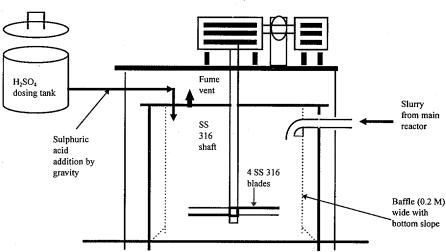


Figure 3.2 Chrome Slurry Redissolving tank

suitable reduction gear box through a flexible bush and pin coupling. Resultant output speed is 40-50rpm. The diameter of the shaft shall be designed taking into account axial and radial load on the output shaft. The base plate for fixing the stirring system is in mild steel channels with FRP coating. All fasteners are in stainless steel. Heavy duty bearings for the coupling guards are provided at the output side of the shaft. It is recommended to have 2 sets of bearings and 6 sets of bushes supplied as spares.

3.5 CHROME REGENERATION TANK

The chrome regeneration tank has a capacity of 1.5 cubic meter. The tank is made of FRP/polypropylene, which can resist acidity of pH below 2 and temperature of 80°C. The tank has provision for a stirrer, acid addition, fume vent, with a top cover in two halves. Four baffles, each 0.2 meter wide, are equally placed inside the tank to prevent formation of vortex (Figure 3.2).

3.6 STIRRER FOR CHROME REGENERATION TANK

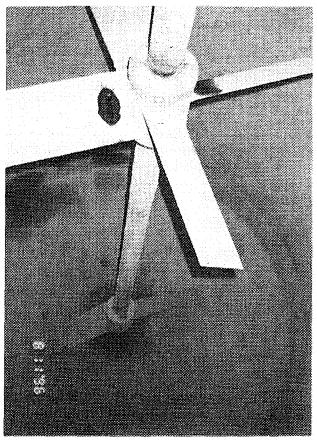
The shaft and the four blades of the stirrer are in stainless steel, (Figure 3.2). The stirrer is driven by a motor coupled to a suitable reduction gear box through a flexible bush and pin coupling. Resultant output speed is 40 - 50 rpm. The diameter of the shaft shall be designed taking into account axial and radial load on the output shaft. The base plate for fixing the stirring system is in mild steel channels with FRP coating. All fasteners are in stainless steel. Heavy duty bearings for the coupling guards are provided at the output side of the shaft.

3.7 MAGNESIUM OXIDE DOSING TANK

100 litres capacity FRP/Polypropylene tank (5-6 mm thick) for MgO solution preparation. A polypropylene ball valve is fixed at the bottom outlet. A support structure with top opening for stirring/manual mixing and cleaning (so that MgO can flow by gravity into the main reactor) is recommended.

3.8 STIRRER FOR MAGNESIUM OXIDE TANK

The shaft and the blade of the stirrer are in stainless steel. The stirrer is driven by a motor coupled to a suitable reduction gear box through a flexible bush and pin coupling. Resultant output speed is 40 - 50 rpm taking into account axial and radial load on the output shaft. The base plate, fixing frame are in mild steel channels with FRP coating. All fasteners are in stainless steel. Heavy duty bearings for the coupling guards are provided at the output side of the shaft.



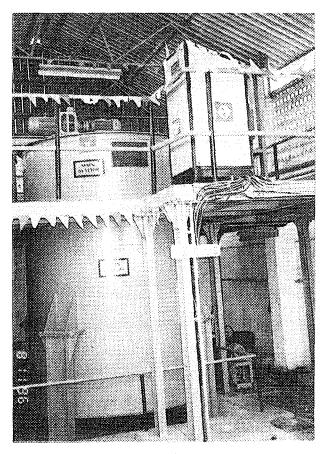
Main reactor (inside view)

3.9 SULPHURIC ACID DOSING TANK

A polypropylene tank for storing and dosing sulphuric acid, 100 litres capacity, fitted with an outlet of stainless steel pipe with FRP coating and valves, is required.

3.10 OPTIONAL SULPHURIC ACID PUMP

An electromagnetic pump with a capacity of 400 litres per hour to pump commercial grade concentrated sulphuric acid from the carboys to the sulphuric acid storage tank can be fixed as an optional item to avoid manual handling of sulphuric acid. The pump is driven by a motor, of class "F' insulation.



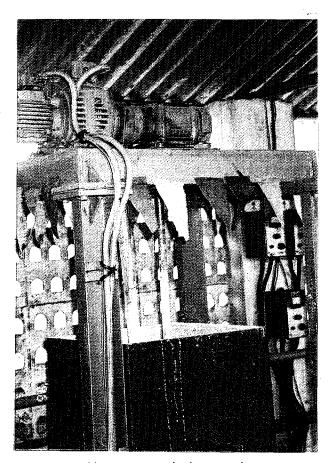
Main reactor (front view)

3.11 RECOVERED CHROME STORAGE TANK

The regenerated chrome liquor storage tank has a capacity of 2 m³. It is made of FRP / HDPE. It has a removable lid at the top and bottom outlet with polypropylene ball valve for pipe connection and chrome liquor distribution. A level indicator must be provided.

3.12 CHROME EFFLUENT TRANSFER PUMP

Two screw pumps (one standby) each with a capacity of 12-15 m³ per hour at 12 meter head capable of handling effluent with a pH of 3 and particles up to a size of 10 mm is required to pump the exhaust chrome liquor from collection tank to main reactor. All the wetted parts shall be in stainless steel and the stator is made of special rubber including glands packing arrangement. The suction and



Magnesium oxide dosing tank

delivery ends are with flange connections. The suction line has a foot valve and strainer. The pump is driven by a motor of class "F' insulation. The baseplate is of mild steel placed over mild steel channels / angles with FRP coating. All the fasteners are in stainless steel.

3.13 REGENERATED CHROME PUMP

Two screw pumps (one standby) each with a capacity of 2-3 m³ per hour at 7 - 8 meter head, capable of handling effluent with a pH of 2 and particles up to a size of 5 mm, is required to pump the recovered chrome liquor to the storage tank. All the wetted parts shall be in stainless steel and the stator is made of special rubber. The suction

and delivery ends are with flange connections. The bottom of the suction line has a foot valve and strainer. The pump is driven by a motor of class "F' insulation, mild steel base plate placed over mild steel channels / angles with FRP coating. All fasteners are in stainless steel.

3.14 SAFETY MEASURES

Normal safety measures as applicable for chemical handling and operation of electrical and mechanical equipment must be taken. Special safety measures are needed when handling concentrated sulphuric acid. High temperature and fumes are likely to be generated during the addition of sulphuric acid in the chrome regeneration tank. Please refer to do's and don'ts in Annexure IV.

3.15 SOURCES OF SUPPLY

There are many engineering companies who manufacture/ supply any or all of the above listed machines and equipment. The list given below is only indicative and may be used for reference.

Italprogretti Engineering

Via Lungarno, Pacinotti, 59 A - 56020,

San Romano, Pisa, Italy Tel: 00 39 571 450477 Fax: 00 39 571 450301

SVV Engineering industries

Sipcot industrial complex Hosur, Tamilnadu- 635 126, India

Tel / Fax:00 91 4344 6747

Haskoning

113 / 216 Swaroop Nagar Kanpur 208 002 India Tel :00 91 512 214529

Fax: 00 91 512 214 595

Devotra B.V.

PO Box 201 4600 AE Bergen op Zoom The Netherlands

Tel: 00 31 1642 57084 Fax: 00 31 1642 55408

Hindustan Dorr Oliver

Chakala, Andheri (East), Bombay 400 091, India Tel: 00 91 228325541

Fax: 00 91 228365659

EIMCO KCP Ltd.

105, Victoria Crescent Road Egmore, Madras 600-008, India

Tel: 00 91 44 8279445 Fax: 00 91 44 8271636

INFORMATION ON THE TANNERY

The Arafath tannery in Pallavaram, Madras where the technology has been demonstrated under the UNIDO project US/IND/90/244, has been using the chrome recovery system continuously from September, 1994. It processes daily 3 to 4 tons of wet salted hides and skins up to wet blue stage. The tannery's current capacity utilisation is 100 %. It has sold wet blue leather, in a period of 2 years, worth US \$ 1.5 million using recovered

chromium. The chrome recovery and re-use system in this tannery has been installed as a common system for selected tanneries in the Pallavaram cluster processing raw hides and skins using chromium. Therefore, the capacity of the system is larger than appropriate for an individual unit processing 3 - 4 tons. The technology package has been designed on the basis of a tannery processing 6 - 10 tons of raw hides / skins per day from raw to finish.



LAYOUT

It is recommended that the chrome recovery and re-use system is built as close as possible to the tanning yard. This is to minimise the drainage / pipeline for collection of spent chrome liquor and to minimise the carrying distance of the recovered chrome to the tanning yard. A second important element is that the spent chrome liquor from the drum should flow by gravity into the spent chrome liquor collection tank. From there it is pumped into the main reactor, and after reaction, the chrome

slurry flows by gravity into chrome regeneration tank. From this tank it is pumped to the recovered chrome storage tank and sent back to the main tanning yard by pipe or buckets as the volume of the recovered chrome liquoris less than 10 % of the total spent chrome liquor processed. The flow of magnesium oxide solution and sulphuric acid are preferably done by gravity so as to minimise the number of pumps needed. Typical lay out and relevant figures are given in Annexure III.



CIVIL WORKS

The following civil works have to be carried out as shown in the figures in Annexure III.

- Water tight collection tank for exhaust chrome liquor storage. The capacity should be at least twice the quantity of chrome liquor estimated to be discharged by the tannery every day and minimal 50 % larger than the capacity of main reactor
- Drainage system for the collection of segregated All interconnections are in PVC / HDPE and valves are exhaust chrome liquor from the chrome tanning drum
- to the collection system generally by PVC pipes of 150mm dia, 6kg/cm² pressure and sufficient length.
- · A new covered shed of an area of 70 sq. m. with working platform of about 20 sq. m. at an height of 2.5 m above floor level for the installation of chrome recovery system for the stated capacity or the existing shed, if any, near the chrome tan yard can be used.
 - in polypropylene



ELECTRICAL INSTALLATIONS

The total power required for the installation of the chrome recovery system designed is 15 KVA in 3 phase, including the requirement for the standby motor and pump sets. A separate panel

board with proper control switches is provided in the plant. The details of the pump sets, stirrers and electrical installations have been given in Annexure II.

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OPERATIONAL INSTRUCTIONS

8.1 TRIAL RUN

- * Procure the specified quality MgO (commercial grade calcined magnesite special white powder 200 mesh) sufficient for at least one month.
- * Commercial grade sulphuric acid (H₂SO₄) normally used in the tannery can be used for chrome regeneration. Test all the units, valves, etc. for water tightness and free flow using water to rinse the main reactor, regeneration tank, storage tank, etc.
- * Discharge exhaust chrome liquor in collection tank to carry out the first two trials to estimate the time of operation, chemicals required, quality of the recovered chromium, etc. .Use the recovered chromium in the experimental drum with one or two pieces of hides/skins to assess the quality of wet blue produced.
- * From the third trial onwards reuse of chromium can be done in the main chrome tanning drums.
 - The total time required for one complete batch operation (i.e.) precipitation, settling and regeneration, is about 8 hours. Two batches can be done in a day depending upon the local conditions. Chronological steps in the process of chrome recovery are given below:
- * End of normal chrome tanning operation in the drum.
- * Remove the conventional door from drum and replace it with the special drumdoor.
- * Fix the flexible hose pipe and connect it to the collection trap connected to collection tank.
- * Turn the chrome tanning drum and discharge the spent chrome liquor to the collection tank (About 10% of the spent chrome liquor will be retained in the drum with hides / skins unless these are washed and discharged again).
- * Collect and store the exhaust chrome liquor in the collection tank till quantity equals the reactor capacity.
- * Pump the exhaust chrome liquor from collection tank to main reactor upto a level of 20 cm below overflow pipe
- * Collect required MgO for one batch and prepare MgO solution by addition of water in the ratio of 1:20 in a container. 20 35 kgs of MgO is needed for about 9,000 litres of exhaust chrome liquor depending upon the chromium concentration and quality of MgO.
- * Operate the main reactor stirrer at 40-50 rpm.

- * Add MgO solution slowly through screen in the main reactor under stirring condition.
- ** Check the pH of the solution in the main reactor during addition of the MgO till the pH reaches 8.0 (i.e. the pH increase will be slow since MgO is a slow reacting alkali). In the initial stages of operation, pH may be checked every 10 minutes, whereas at a later stage after gaining operational experience less frequent checking is needed.
- * Operate the stirrer for 1 hour and then stop
- * Allow settling of precipitated chromium for 4 hours
- * Decant the supernatant through side valves one by one from top to bottom by checking clarity
- * Close all the side valves after discharge of supernatant
- ** Operate the main reactor stirrer for 5 minutes at 40 50 rpm or if a variable speed option is available at 10 20 rpm.
- * Open the bottom valve slowly and empty the chrome slurry to chrome regeneration tank provided at bottom. Close bottom valve and stop main reactor stirrer
- ** Start the stirrer in chrome regeneration tank. Add sulphuric acid (required amount is 30 50 litres for 700 litres of chrome slurry) slowly till the pH reaches 2.5 2.8 range and check temperature. Watch for any fumes and do not touch the liquor by hand
- * Stir for 1 hour and check if the pH has increased to about 2.8 and basicity 30 % to 33 %, then stop stirrer in regeneration tank
- * Allow for natural cooling for 3-4 hours. Pump the recovered chrome liquor from bottom tank to chrome storage tank
- * Collect recovered chrome liquor in buckets from pipe line leading from recovered chrome storage tank and add into tanning drum along with required amount of fresh chrome to suit field condition
- * After completion of chrome tanning operation in drums, repeat the process.

8.2 LEATHER QUALITY, PHYSICAL & CHEMICAL PROPERTIES

The main physical properties namely thickness of the leather, tensile strength, tear strength and water penetration were tested. The tests were carried out in accordance with IUP (International Union Physical) and

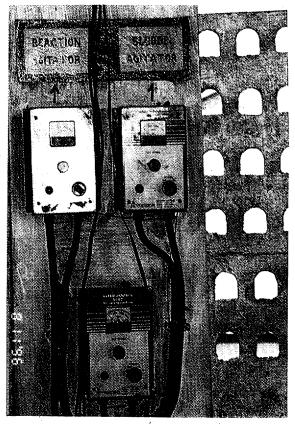
BIS (Bureau of Indian Standards). Relevant chemical properties namely moisture, chromium, chlorides, sulphates and MgO contents of both types of leathers, viz. one processed with fresh chromium and another processed with fresh and recovered chromium in the ratio 70: 30, on all the sides were tested. From the chemical properties it is established that the two types of leathers are similar.

8.3 ORGANOLEPTIC LEATHER QUALITY

The different aspects of the organoleptic quality, viz. grain tightness, softness and fullness, tightness of bellies, grain drawiness, veininess, eveness of colour, have been compared for the normal tanning processes using fresh BCS only and tanning process using 70% fresh BCS and 30% recovered chromium. The leather tanned with recovered chromium is of similar quality as the leather tanned with 100% fresh chromium.

8.4 OCCUPATIONAL SAFETY AND HEALTH MEASURES

This aspect is detailed in Annexure IV. "Do's and Don'ts" in a chrome recovery plant must be displayed prominently in vernacular language for the benefit of workers.

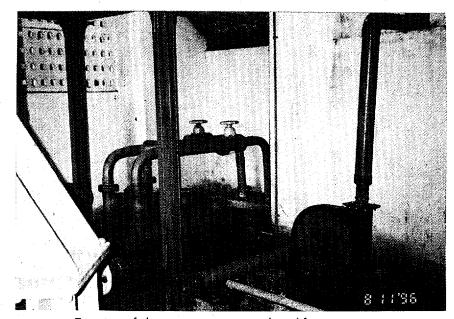


Control panel for agitators

9

COST BENEFIT ANALYSIS

The entire chromium discharged in the collected effluent is recovered and used. Processing of hides and skins both before and after the main tanning operations remains the same in terms of processing time and method. Because the quality of leather is not affected, the commercial value of the leather is not changed. Hence, the cost benefit analysis will be restricted to: investment **cost** for chrome recovery system, the operating **cost**; and **benefit** in the form of the chemical saved. The benefit however does not take into account any saving in reduction of cost of effluent treatment or disposal of sludge.



Top view of chrome regeneration tank and fume extraction

Chrome tanning capacity	3000 tons of hides/skins per year
Use of chromium salt (BCS)	240 tons/year.
Wastage of chromium salt (BCS)	80 tons/year.
Cost towards civil works (drainage, collection tank and platform)	US \$ 8,000
Equipment and erection	US \$ 50,000
Miscellaneous expenses	US \$ 2,000
Total capital cost of the chrome recovery system	US \$ 60,000
ANNUAL OPERATING COST	COST IN US DOLLARS
Maintenance	1,000
Labour	1,000
Chemicals	6,000
Electricity	500
Miscellaneous	1,500
Total annual operating cost	10,000
Cost of finance (15 % p.a.)	9,000
Depreciation (15 % p.a.)	9,000
Total annual cost	28,000
BENEFIT	
Value of chromium recovered @ about US \$ 800 per ton for 70 tons	US \$ 56,000
Net profit per year	US \$ 28,000

Cost benefit analysis based on the chrome recovery system at Arafath Leathers, India

From the cost benefit analysis it may be observed that the total cost of recovered chromium is less than US \$ 400 per ton whereas the fresh chromium salt costs more than US \$ 800 per ton. The pay back period of the whole chrome recovery plant is less than three years. In addition

to direct financial benefit, the operation and maintenance cost of the effluent treatment plant in respect of chemical usage and disposal of chrome containing sludge will be considerably reduced.

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10

GENERAL GUIDELINES

- 10.1 Traditional tanning is not very well controlled and the nature of the chromium salt and the conditions used for tanning are such that at the end of the tanning the spent liquor contains 30-40% of the chromium salt applied in the process. In traditional chrome tanning about 100% water on the basis of hide/skin pelt weight, 6-8% BCS, and 2% sulphuric acid are added and the drum is operated for 5-7 hours. The exhaust liquor is discharged as waste and the hides/skins after this operation are called wet blue (semi finished leather). The wet blue is further processed to produce finished leather.
- 10.2 In some tanning systems, it is possible to decrease the chromium content in the waste liquor to less than 15% of the chromium applied by using improved drums, special chemicals and process control. Therefore, a thorough study needs to be made of the available chrome management systems, viz. direct recycling, high exhaust chromium, chromium substitutes and chrome recovery and reuse. A techno-economic survey of all these methods individually or in combination will give the tannery the necessary data for taking a decision.
- 10.3 In case the tannery decides to install a chrome recovery and re-use system, it is important that a survey is made on the prevalent chrome tanning practices in the tannery i.e. percentage of chromium used, float, operation time, wastewater and chromium content in the waste water. The chromium content as Cr in the exhaust chrome discharge may range from 1,500 to 5,000 mg/l in the discharge from main chrome tanning drums and 500-1500 mg/l in case of rechrome tanning. This is due to differences in raw material quality, chemical and volume of water used in individual lots.
- 10.4 Periodical analysis of the exhaust liquor is necessary to estimate the required amount of MgO and sulphuric acid for the recovery process. A log book should be maintained in the plant with the following data:

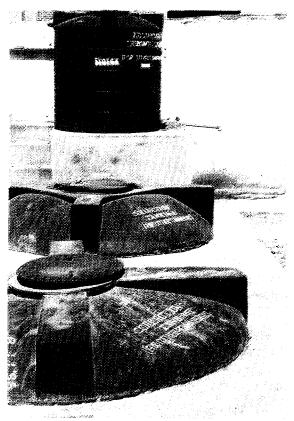
Date and volume of exhaust chrome liquor processed in the main reactor

Quantity of MgO used (generally 20-35 kgs. for each batch of 9,000 liters capacity)

Volume of sulphuric acid used (generally 30-50 litres per lot of about 700 litres of chrome slurry).

The basicity and concentration of recovered chromium (generally ranges from 30-33% and 100 litres of recovered chrome liquor is generally equivalent to 20-25 kgs. of BCS available in the market).

Ratio of fresh BCS and recovered chromium application (generally for one lot of chrome tanning with 1000 kgs. pelt with required float,55 kg of BCS (5.5% on pelt weight) and 100 litres of recovered chrome liquor generally equivalent to 25 kgs. of BCS are added. Thus the total chromium input is equivalent to 80 kgs. of normal BCS).



Collection tanks for common chrome recovery system

10.5 The precipitated chrome slurry is less than 10% of exhaust chrome liquor volume and the supernatant, which is about 90%, is decanted and used for first soaking operation. Therefore, a significant amount of dissolved solids is removed along with the decanted supernatant liquor. The supernatant may be reused in the soaking operation and partly (50 %) in pickling, without any difficulty.

10.6 CONSTRAINTS AND TECHNICAL CONSIDERATIONS

Though there is no major technical constraint in adopting the chrome recovery and reuse system with MgO as alkali sufficient attention should be paid to the following:

- * MgO is a slow reacting alkali and the pH increases slowly after the addition of MgO for chromium precipitation. Hence, time required for MgO addition is comparatively more to achieve the desired pH. The possibility of excess addition of MgO, considering the initial indication of pH,is a common error.
- * The main reactor particularly the bottom slope and stirring system should be properly designed on a case to case basis to avoid any choking or accumulation of chrome slurry in the reactor.
- * Precaution must be taken against acid fumes while adding concentrated sulphuric acid during the regeneration of chromium. Fume vents must be provided.
- * Periodical testing is required on the quality of exhaust chromium, MgO and H₂SO₄ requirement and Cr₂O₃ content in the recovered chrome liquor.
- * Regular pH measurement and periodical chromium and basicity estimation are necessary to estimate the required quantity of chemicals used in the recovery process and also for the reuse along with fresh BCS.
- * By using the chrome recovery and reuse system there may be a slight increase of magnesium and dissolved solids. This will become significant if the supernatant is not reused for soaking/pickling.

- ** Foam formation is likely to occur in the main reactor during the recovery process using the exhaust chrome liquor from rechroming since some tanneries use different solvents, detergents and foaming agents. This may be tackled by either slowly pumping the exhaust chrome liquors in the main reactor or by using one of the supernatant drain valves as an inlet for the exhaust chrome liquor.
- 10.7 The operators of the chrome recovery and reuse system have to be trained in sample collection, analysis, operation and maintenance of the chrome recovery and reuse system. They must be able to understand and utilize the system regularly. A list of Do's and Don'ts may be seen at Annexure IV.
- 10.8 This system cannot claim to recover all chromium from the waste, unless chrome containing liquor from retanning/rechroming process is also processed for recovery of chrome, in tanneries processing from raw to finishing. Invariably, as the chrome content in the exhaust chrome liquor from rechroming is low, this is not generally collected for recovery of chrome. And if the tannery is processing only semi-finished leather into finished leather, it may not be economically attractive.

ANNEXURE I

CHROME RECOVERY AND REUSE SYSTEM (Capacity: 9000 litres/Batch)

ACTIVITIES FOR IMPLEMENTATION (Ref. Annexures II & III)

S. No.	Activity	Role of turnkey implementing agency	Role of tannery / civil works contractor
A)	Exhaust chrome liquor discharge conveyance and collection system		
i)	Special drum door with screens, hydrant valves, hose pipe with coupling nozzles - 3 sets	Yes	
ii)	PVC Pipeline (15 cm dia) 6kg/cm ³ from chrome tan yard including excavation, laying, jointing, base cement concrete below and at top of pipeline in tannery and pumping, if necessary upto exhaust chrome liquor collection tank	·	Yes
iii)	Inlet/junction chamber 0.5 m length x 0.5 m width x 0.3 m depth or 20 cm dia cylindrical screens for collection system to suit local condition with stainless steel /FRP sieve cages (total 4 to 5 numbers)		
	Supply of FRP sieve cage	Yes	
	Fixing		Yes
iv)	Providing screen chamber 1 no of size 2.0 m long x 0.75 m width x 0.6 m depth approximate (likely to vary) to suit site conditions, at the inlet point of the collection tank		Yes
	Supply of stainless steel screen	Yes	
В)	Exhaust chrome liquor collection tank (15 m3 effective capacity and water tight) excavation, PCC, brick work/concrete, plastering, cover slab etc. to suit local condition		Yes
(C)	Machine foundation work for main reaction tank excavation, PCC flooring, RCC foundation for reaction tank, PCC foundation for platform support, etc.		Yes
D)	Supply and erection of special reaction tank of 9 cubic meter per batch, MS plates/FRP, angles, supporting columns, supernatant decanting valves, sludge removal valve and pipeline stirrer assembly and stirrer, platforms, foundation bolts, etc. including erection.	Yes	

S. No.	Activity	Role of turnkey implementing agency	Role of tannery / civil works contractor
E)	1.5 cubic meter chrome slurry dissolving tank, FRP/polypropylene, stirrer assembly with SS 316 shaft and blades, sulphuric acid addition system, etc.	Yes	_
F)	Pumping system with special pumpsets (2+2) and inter-connections	Yes	
G)	Working platform with stair and handrails		Yes
H) -	Recovered chrome collection and distribution system		
	i) 2 cubic meter capacity recovered chrome liquor storage tank (1)	Yes	<u>—</u>
	ii) Distribution to drums with 50-63 mm dia HDPE/PVC line at about 2.5 m above G.L with ball valves. Alternatively the recovered chrome liquor can be collected in small containers of 30-50 litres capacity and shifted to chrome tanning yard for reuse		
· I)	Electrical/Instrumentation	*	
	(i) Upto main panel at chrome recovery system	_	Yes
·	(ii) Providing control panel and interconnections for chrome recovery system	Yes	
J)	Covered shed of about 70m ² area for the plant with water supply (i.e. 200 litres per day) and lighting. (existing tannery shed may also be used)	-	Yes
K)	Raw material, chemical, consumable (water, power) etc. for chrome recovery system	· —	Yes
L)	Trial run, standardisation, training, etc.	Joint activity	Joint activity

ANNEXURE II

CHROME RECOVERY SYSTEM CAPACITY: 9 CUBIC METER/BATCH

EQUIPMENT SPECIFICATION (Ref. figures in Annexure III)

Item	Quantity	Specification
1 a	1 no.	Stainless steel (SS 316) screen with perforated holes and size to suit the screen chamber of size 2.0 long x 0.75 wide x 0.6 m depth as shown in fig. Screen shall be provided with a handle at the top to facilitate the lifting of the screen from the screen chamber and "U" shaped S.S. rails for sliding of the screen into the chamber. Welded joints shall be given FRP coating. Thickness of the screen shall be min 3 mm and the frame shall be min 6 mm.
1 b	4 nos.	Stainless steel (SS316) screen of size $0.5 \text{ m} \times 0.5 \text{ m} \times 0.5 \text{ m}$ with SS bar suitably welded and to be fixed in the drum doors approximate 15% smaller than the drum door.
'1 c	5 nos.	Cylindrical screens in FRP of size of 0.15 m dia x 0.2 m depth with perforated holes in the bottom and side to be fixed in the collection drain.
1 d	4 nos.	Fire hydrant type valves of 50mm dia in brass.
1 e	4 nos.	Flexible PVC hose of 63 mm dia (OD) for length of 10 meters each.
1 f	1 no.	Basket screen (SS 316) length x width x depth = $0.4 \times 0.4 \times 0.2$ meter, mesh size 2-3 mm.
2.	2 nos.	CHROME EFFLUENT TRANSFER PUMP SET
		Screw pump capacity 12-15 cubic meter/hr at 12m head to transfer the chrome effluent from the collection tank to reactor. Pumps shall be capable of handling effluent with a pH of 3 and particles of upto 10mm. All wetted parts like shaft, rotor, pump housing etc., shall be in SS 316 and stator shall be made of viton rubber. Suitable gland packing arrangement shall be provided. Suction and delivery ends shall be of flange connection and conforming to BS 10, table D standards or equivalent national standards. Suction line shall be provided with a foot valve and strainer. Each pump shall be driven by a suitable totally enclosed fan cooled, IP 55 motor of class "F" insulation. Pumps shall be provided with a base plate of 6 mm thick mild steel placed over MS (mild steel) channels/angles with FR P coating. All the fasteners shall be in SS 316. MAKE: ALWEILER TUSHACO/ROTO/ROTOMAC/ALPHA HELICAL (OR) EQUIVALENT REPUTED MAKE
3 a	1 no.	MAIN REACTOR Main reactor of size 2.0 m dia x 3.0 m TD for a capacity of 9000 litres shall be installed for the reaction of chrome liquor. Made of flat sheet mild steel 6-8 mm thick with FRP lining in 3 layers each of 1 mm thick using biphenol resin and epoxy inside and one layer FRP with surface mat outside bottom slope between 5-15°. The reactor shall be supplied with 4 supporting columns in heavy duty mild steel angle of 2.2 to 2.8 m height and fitted with base plate, fixers, cross angles. All connections with necessary bolts and nuts in SS 316, including 4 nos polypropylene anticorrosive ball valves of 50-80 mm dia and provision for overflow discharge at top side. Provision for chrome slurry withdrawal with a cast iron (CI) sluice valve of 125-150 mm with stainless steel (SS 316) internal parts at the reactor bottom shall be provided. The reactor shall be generally as per drawings in Annexure III. All flanges shall be conforming to BS 10 table D standards.

Item	Quantity	Specification
3b	1 no.	STIRRER FOR MAIN REACTOR Stirrer shall be installed in the main reactor for mixing of chrome liquor and precipitation using MgO. The stirrer shaft shall be in Stainless Steel (SS 316) for a length of about 3.3 m with SS 316 blades - one at the middle and the other in the bottom as shown in the drawings (Annexure III). The stirrer shall be driven by a suitable totally enclosed fan cooled (TEFC), IP 55 motor of class "F' insulation coupled to a worm reduction gear box through a flexible bush and pin coupling for a resultant output speed of 40rpm. The base plate for fixing the stirrer system shall be in M.S. channels with FRP coating. All the fasteners shall be in stainless steel (SS 316). Gear box shall be selected taking into consideration the axial load and radial load on output shaft. Suitable coupling guards shall be provided with heavy duty bearings at the output side of the shaft. 1 set of bearing and 2 sets of bushes suitable for the stirrer shall be supplied as spares. MAKE: MOTORS: KIRLOSKAR/ABB/SIEMENS/CROMPTON/EQUIVALENT GEAR BOX: RADICON/ESSENPRO/EQUIVALENT
4a	1 no.	CHROME REGENERATION TANK Chrome regeneration tank of capacity 1.5m ³ shall be provided for the chrome slurry discharged from main reactor. A circular tank of about 1.4 m dia shall be made of 6-8 mm thick FRP with bisphenol resin which can resist acids of pH below 2 and high temperature of 80°C with provision for stirrer, acid addition, fume vent, top cover in two halves, etc. complete with a gentle slope at the bottom. Four baffles each of 0.2 meter wide are equally placed inside the tank. The baffles will have a slope in the bottom of about 45°.
4b	1 no.	STIRRER FOR REGENERATION TANK The shaft and blade of the stirrer shall be in stainless steel (SS 316) and driven by totally enclosed fan cooled IP 55 Motor of class "F" insulation coupled to a suitable worm reduction gear box through a flexible bush and pin coupling of reputed make for a resultant output speed of 40-50 rpm. Base plate and fixing frame shall in (mild steel) M.S. with FRP coating as shown in the enclosed drawings. All the fasteners shall be in stainless steel (S.S. 316). Gear box shall be selected taking into consideration the axial load and the radial load in the output shaft. Suitable coupling guards shall be provided. 1 set of bearing and 3 sets of bushes suitable for the stirrer shall be supplied as spares. MAKE: MOTORS:KIRLOSKAR/ABB/SIEMENS/CROMPTON/EQUIVALENT GEAR BOX: RADICON/ESSENPRO/EQUIVALENT
5.	2 nos.	Screw pumps each of capacity 3m³/hr at 7-8 m head shall be provided to transfer the regenerated chrome from the regeneration tank to recovered chrome storage tank. The pumps shall be capable of handling liquids with a pH of 2 and particles of upto 5mm. All the wetted parts like shaft, rotor, pump housing etc. shall be in SS 316 and the stator shall be made of viton rubber. The suction and delivery ends shall be of flange connections conforming to BS 10 table D standards. A foot valve with a strainer shall be provided at the bottom of the suction totally enclosed fan cooled, IP 55, Motor of class F insulation. Each pump shall be provided with a base plate of 16mm thick mild steel placed over M.S. channels/angles with FRP coating. All the fasteners shall be in stainless steel. (SS 316). One set of spares (stator, rotor shaft, gland packing and 0-rings) suitable for the pumps shall be supplied. MAKE: ALWEILER TUSHACO/ROTOMAC/ALPHA/ROTO HELICAL/EQUIVALENT

Item	Quantity	Specification
6.	1 no.	RECOVERED CHROME STORAGE TANK FRP/HDPE tank /2000 litres capacity shall be provided for storing the recovered chrome. The tank shall be of 6 mm thick FRP (coated with bisphenol resin)/HDPE. The tank shall have removable lid and bottom outlets with Polypropylene valve of 50 mm dia for pipe connections for chrome liquor distribution. Provision need to be made in the tank for hanging SS basket screen at the inlet pipeline. Level indicator shall be provided for the tank.
7 a	2 nos.	SUPLHURIC ACID STORAGE TANK Storage tanks of 100 litres capacity shall be provided for storing and dosing the sulphuric acid. The tank shall be made of PP with 6 mm thick for acid storage. Each tank shall be fitted with an outlet of Stainless Steel pipe of size 25–50 mm dia with FRP coating and necessary valves shall be provided.
7 b	1 no.	SUPLHURIC ACID PUMP (OPTIONAL) Electro mechanical pump of capacity 400 litres/hour shall be provided to pump the commercial grade conc. sulphuric acid from the carboys to the sulphuric acid storage tank. The unit shall consist of Cl base with aluminium housing with FRP coating, Cl spacer, PP head, Diaphragm in Teflon faced hypalon, Valve ball in ceramic, Valve ring seal in Teflon and Fitting in PP/PVC. Each pump shall be driven by suitably Totally Enclosed Fan Cooled, IP 55 motor of class F insulation. 1 set of Ring seals, Diaphragm for the pump shall be supplied as spares. MAKE: MILTION ROY/PROMINENTIPLUNGER/EQUIVALENT
8a	1 no.	MAGNESIUM OXIDE DOSING TANK Cylindrical tank of 100 lit capacity shall be of FRP/PP. The tank shall be provided with Polypropylene ball valve of size 25 mm at the bottom outlet. A suitable support need to be provided for placing the MgO tank for the gravity flow of MgO solution to the main reactor.
8 b	1 no.	STIRRER FOR MAGNESIUM OXIDE DOSING TANK Stirrer with shaft and blade shall be in stainless steel (SS 316). The stirrer shall be driven by a suitable Totally Enclosed Fan Cooled, IP 55 Motor of Class F insulation coupled to a suitable worm reduction gear box through a flexible bush and pin coupling of reputed make for a resultant output speed of 40–50 rpm. The base plate and fixing frame shall be in M.S. with FRP coating. All the fasteners shall be in Stainless Steel (SS 316). The gear box shall be selected taking into consideration the axial load and the radial load in the output shaft. Suitable coupling guards shall be provided. Alternatively suitable geared motor with 40–50 rpm can be provided. 1 set of bearings and 2 sets of bushes for the stirrer shall be supplied as spares. MAKE: MOTORS: KRILOSKAR/ABB/SIEMENS/CROMPTON GEAR BOX:RADICON/ESSENPRO/EQUIVALENT

Item	Quantity	Specification		
9	1 lot	PIPING AND VALVES		
		All interconnecting piping and valves as specified in equipment specifications and as per the enclosed and drawings (Annexure III) shall be provided. All piping materials shall be in PVC/HDPE and valves shall be in P.P. All the piping works shall be executed to suit the local conditions.		
10	1 lot	ELECTRICALS		
		Providing all electrical installations (3 phase) required for the chrome recovery unit such as copper cables, starters, switches, push button stations, control panel 15 KVA with incomer switch as changeover switch for the total chrome recovery unit shall be supplied. All the electrical items shall be of reputed make in conformity to BS or equivalent national standards.		
11	1 lot	GENERAL ITEMS		
		A name board using aluminium panel showing process flow diagram and layout of the chrome recovery unit shall be provided at the plant. The board shall be of size 1.2 m x 0.9m. The flowsheet and layout shall be screen printed on an Acrylic Sheet framed with aluminium support.		

Note

SWD	Side Water Depth	IP	Insulation & Protection
TD	Total Depth	HDPE	High Density Poly Ethylene
SS	Stainless Steel	LDPE	Low Density Poly Ethylene
MS	Mild Steel	FRP	Fibre Reinforced Plastic
\mathbf{PP}	Polypropylene	mm	Millimetre
CI	Cast Iron	m	Meter
PVC	Poly Vinyl Chloride	no.	number
BS	British Standards	nos.	numbers
BIS	Bureau of Indian Standards	rpm	rotations per minute
GI	Galvanised Iron	-	•

ANNEXURE III

DETAILED DRAWINGS OF

FIG 1. PROCESS FLOW DIAGRAM

FIG 2. TYPICAL LAYOUT

FIG 3. LEVEL INDICATION FOR CIVIL AND MECHANICAL WORKS

FIG 4. DETAILS OF COLLECTION TANK

FIG 5. DETAILS OF SCREEN CHAMBER

FIG 6. PIPELINE ARRANGEMENT DIAGRAM

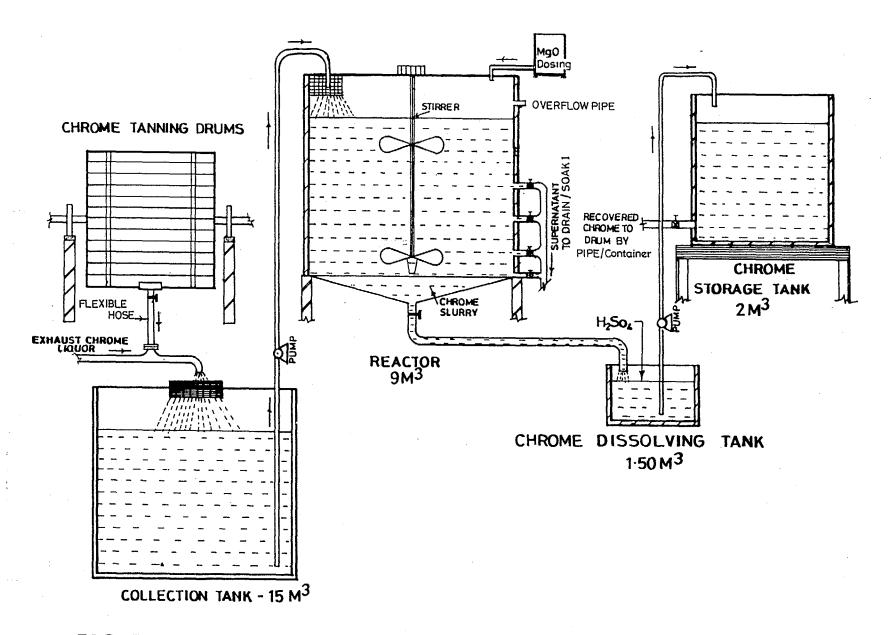


FIG.1 - PROCESS FLOW DIAGRAM FOR CHROME RECOVERY

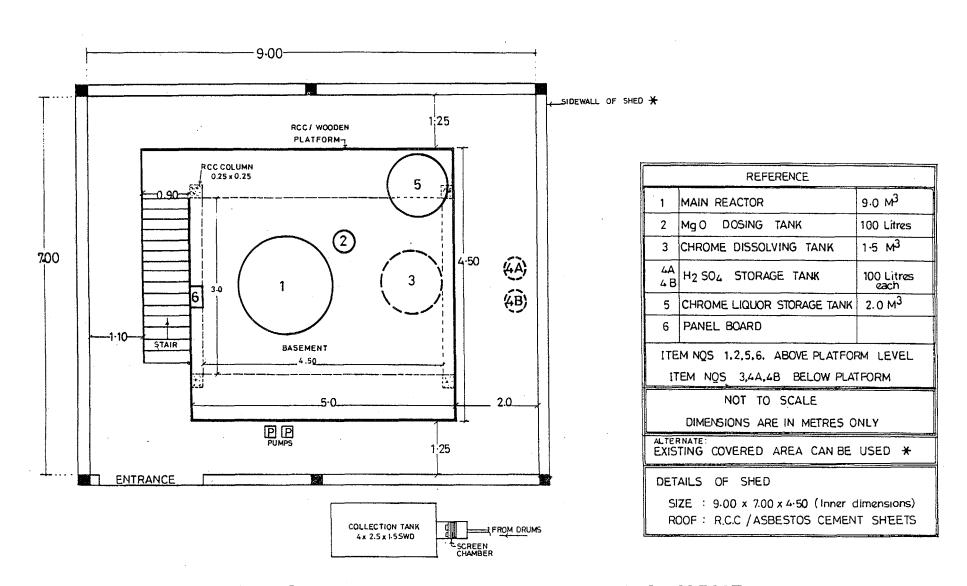


FIG.2 - TYPICAL LAYOUT ARRANGEMENT

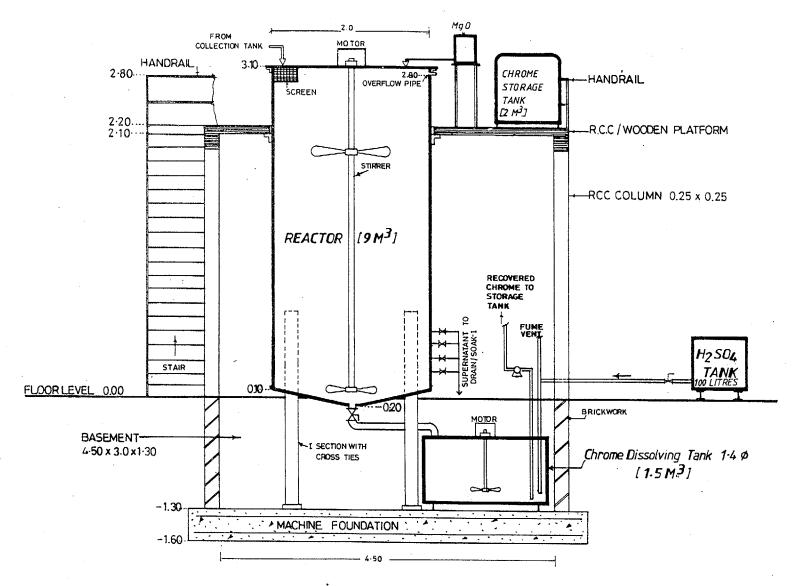


FIG.3 - LEVEL INDICATION FOR CIVIL, MECHANICAL WORKS

(Note: Not to Scale / Dimensions & Levels in Metres)

DIMENSIONS AND LEVELS IN METRES SUBJECT TO SUIT SITE CONDITIONS

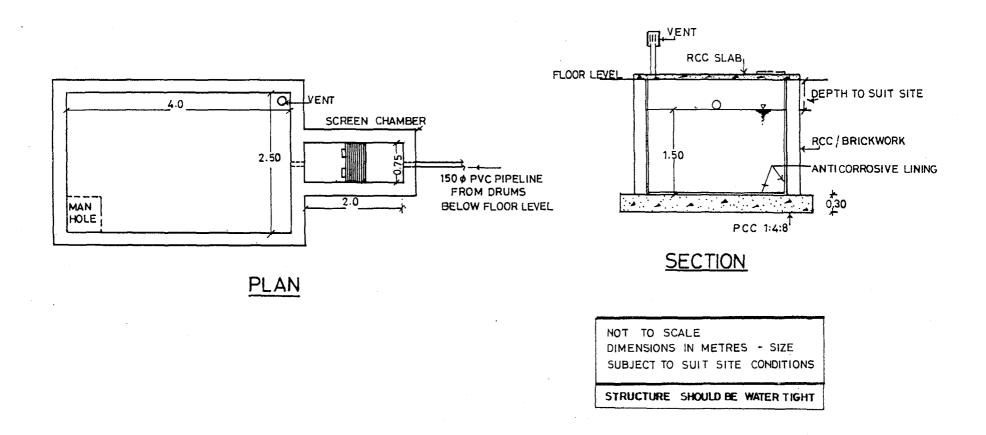
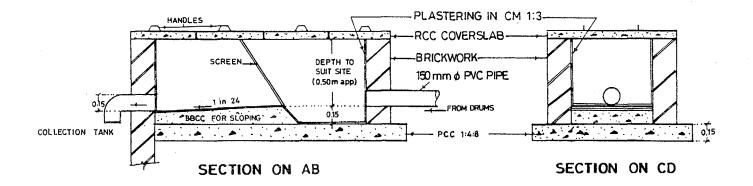


FIG.4 - DETAILS OF COLLECTION TANK



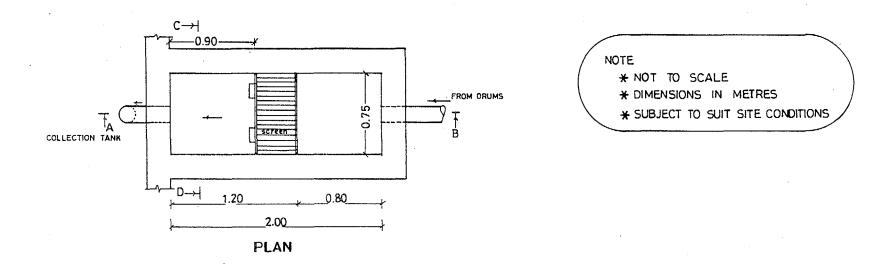


FIG.5 - DETAILS OF SCREEN CHAMBER

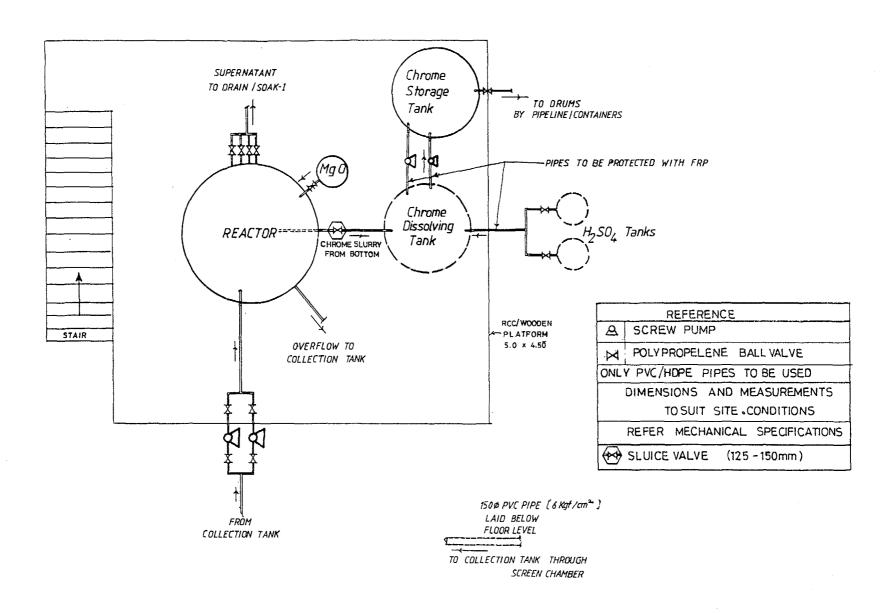


FIG.6 - INDICATIVE PIPELINE ARRANGEMENT

ANNEXURE IV

CHROME RECOVERY AND REUSE SYSTEM

"DO'S AND DON'TS"

- Maintain a log book noting the quantity of MgO and sulphuric acid used per batch and operation time of each unit.
- Measure the pH and chromium concentration in the waste chrome liquor and recovered chrome liquor periodically.
- responding the screens, sieve gauge, screen chamber etc. in the collection system every day.
- At least two times in a week, after pumping the regenerated chrome liquor from the bottom tank to the recovered chrome storage tank, switch off all the electrical switches and clean the sediments in the regeneration tank.
- Once in 15 days, after emptying the recovered chrome from the storage tank, remove the sediments.
- Once in three months, during holiday period, empty the main waste chrome liquor collection tank and clean the sediments
- Do not use any stick or hard material to clean the inside portion of the main reactor.
- Check the voltage (440 Volts) before starting pumpsets, stirrer and electrical items.
- Operate only one pump at a time. Do not operate the screw pump when valve is closed in the pipeline
- Provide hand gloves, apron and fume mask to the technicians. Keep a first aid box including medicines for burns caused by H₂SO₄.
- Keep the entire system clean and avoid any obstacles in and around the system. During any major problem or emergency stop all the main switches and contact turnkey contractor or main equipment supplier for technical guidance.

For further details, please contact:

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