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ENZYMATIC DIGESTION OF CHROME SHAVINGS

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LIST OF SYMBOLS AND ABBREVIATIONS

^0C	:	degree Celsius
CLRI	:	Central Leather Research Institute
c_p	:	Specific capacity of hot air
Dwg.	:	Drawing
EI	:	East India (Vegetable) tanned leather
g	:	gram (s)
HDPE	:	High Density Poly Ethylene
IIT	:	Indian Institute of Technology
J	:	Joule
kg	:	Kilogram (s)
kJ	:	Kilo Joule
kW	:	Kilowatt
l	:	Litre(s)
MgO	:	Magnesium Oxide
mm	:	Millimeter (s)
ml	:	Millilitres
min	:	Minute (s)
PH	:	Protein Hydrolyzate
PVA	:	Poly Vinyl Alcohol
PVC	:	Poly Vinyl Chloride
RePO	:	Regional Programme Office of UNIDO at Chennai
Rs.	:	Indian Rupees
TCMTB	:	Thio cyano methyl thio benzothiazole
TKN	:	Total Kjeldahl Nitrogen
UNIDO	:	United Nations Industrial Development Organization

(Rate of exchange: 1 US $ = Rs. 46.80)

EXECUTIVE SUMMARY

Utilization or safe disposal of some solid wastes from tanneries, such as wetblue shavings, continues to pose a serious challenge in many South East Asian countries. While processing one tonne of raw hide / skin, approximately 95 to 100 kg of wetblue shavings are produced. Currently a part of the chrome shavings is used in the manufacture of leather board by combining with shavings of vegetable tanned leather. Unused portion of wetblue shavings is dumped in open areas around tanneries posing a serious environmental hazard.

Conversion of chrome shavings into usable products employing the technique of enzymatic digestion as developed in the United States of America is already practised in a commercial plant in the Czech Republic. The plant has a capacity to process 3 tonnes per day. Three products, namely, gelatable protein, protein hydrolyzate and filter cake are obtained from enzymatic digestion of chrome shavings. While the products obtained find use in construction and plywood industry and also as nitrogenous fertilizer, the chrome-containing filter cake can be used as a reducing agent in the preparation of basic chromium sulphate.

Prof. Karel Kolomaznik of BRNO University was engaged by UNIDO to demonstrate the technology. A series of semi-industrial scale trials were carried out in Chennai, India. A reactor in the chemical engineering department of Central Leather Research Institute (CLRI) was used for digestion. Filtration was done using simple bag type filters. A thin film evaporator & a spray drier in the Indian Institute of Technology Madras (IIT) were used for concentrating and evaporating the filtrate.

This reports covers the activities carried out between May 1999 and September 2000.

The process of enzymatic digestion is done in two stages, namely, denaturation and enzymatic hydrolysis. In denaturation, chrome shavings are digested at pH 9.0 and at a temperature of 70^0C for 3 to 5 hours. After digestion, the hot reaction mixture is filtered and gelatable protein and intermediate filter cake are obtained. The intermediate filter cake is loaded again into the reactor for enzymatic hydrolysis, which is done using a suitable enzyme at the same pH and temperature, for two hours. On filtering the reaction mixture, protein hydrolyzate and filter cake are obtained.

The gelatable protein and protein hydrolyzate obtained in the trials were concentrated to 30% and 50% solid content respectively. The chrome-containing filter cake was used as reducing agent in the preparation of basic chromium sulphate from sodium dichromate in a laboratory scale trial.

The cost of processing one kg of chrome shavings was found to vary from Rs. 2.85 to Rs. 10.55. At the end of the consultant's mission, a meeting with representatives of relevant by-product industry and scientists of CLRI was held to discuss the feasibility of commercial application of this technology in India. The participants felt that while the cost of fertilizer was too high, the option of making other products needed further study particularly with respect to the marketability of these products.

1. INTRODUCTION

In the process of converting raw hides and skins to finished leather, liquid and solid wastes are generated. Management of wastes from tanneries has become important in the developing countries of South East Asia due to increasingly strict environmental regulations. Plants for treatment of liquid waste have been established in many of these countries. Though many options exist for management of solid wastes from tanneries, solid waste utilization and disposal continue to pose a serious challenge to the tanners.

An estimate of solid wastes generated from tanneries is given in table 1.

Table 1: Solid wastes (tanned & untanned) generated while processing ONE tonne of wet salted raw hides

S. No.	Item	Quantity in kg
1.	Raw trimmings	80-120
2.	Hair / Wool	40-50
3.	Wet limed fleshings	250-300
4.	Wetblue trimmings and unusable splits	100-110
5.	Shavings	90-100
6.	Buffing dust	1-2
7.	Crust and finished leather trimmings	9-13

The wetblue leathers are shaved to obtain uniform thickness in the finished leather. This operation in a shaving machine generates wetblue shavings as waste. A part of chrome shavings is used in leather board manufacture. As seen from the above table, approximately 95 kg of wetblue shavings is generated while processing one tonne of raw hides / skins.

The raw trimmings & limed fleshings are used in the manufacture of glue. Fleshings can be converted to animal feed protein.

2. CHROME SHAVINGS - REUSE AND / OR DISPOSAL

As stated earlier, a part of wetblue leather shavings is used in leather board manufacture along with vegetable tanned leather (EI) shavings. The wetblue shavings are mixed with EI shavings in the ratio of 1:2 for production of leather board. Unused wetblue shavings are dumped in open areas around tanneries, riverbeds, etc. in India and elsewhere in the region causing a serious environmental hazard. The presence of chromium in such shavings poses a potential danger.

3. CONCEPT ON ENZYMATIC DIGESTION OF CHROME SHAVINGS

The process of enzymatic digestion of chrome shavings is based on a technology, which was developed in the US Department of Agriculture in Philadelphia. This was employed in TANEX Company, in Hrádek nad Nisou, with a daily capacity to process 3 tonnes of chrome shavings.

This technology uses organic amines such as iso-propyl amine, di-isopropyl amine, cyclo-hexyl amine and other chemicals. Use of these volatile amines has the following advantages:

a. Ash content in hydrolyzed products is low.
b. It increases the chromium oxide content in filter cake, thus facilitating regeneration of tanning salt.
c. When concentrating diluted solutions of protein hydrolyzate, a certain regeneration of organic base i.e. amines takes place.
d. The efficiency of protein yield increases from 60% to 80% and more.

The filter cake obtained from the enzymatic digestion contains chromium oxide and remnant protein. The filter cake is used as a reducing agent in the preparation of basic chromium sulphate from dichromate.

3.1. Description of technology adopted in the industry in Czech Republic

A hydrolysis reactor is dosed with 10 tonne of water, 90 kg of cyclohexylamine or corresponding quantity of iso-propylamine or di-isopropylamine and 60 kg of magnesium oxide. 3 tonnes of chrome shavings are gradually added under constant stirring of the mixture so prepared and heating is started. In the case of cyclo-hexyl amine the heating is started after adding 1.5 tonnes of shavings and in the case of much more volatile isopropyl amine it is started only after adding the whole batch of shavings, i.e. 3 tonnes. If the particle size is large as in the case of wetblue trimmings and splits, it is recommended to allow the reaction mixture to stand overnight with occasional stirring and no heating.

During the process of hydrolysis, checks are run on the optimal (70^0C) temperature and pH (9.0) value. Adjustment of the pH is done by adding organic bases. After a reaction time of 3 – 5 hours, the hot heterogeneous mixture is filtered, the filtrate, which is gelatable protein, is collected in storage tank from where it is pumped into a continuously working three-stage vacuum evaporator.

The filter cake is transferred to a reactor and three tonne of water is added. The pH is adjusted to 9; 0.9 kg of proteolytic enzyme (ALCALASE 2, 5LDX of Novo Nordisk, Denmark) is dosed in and the mixture repeatedly heated under constant stirring for 2 – 3 hours, keeping the maximum temperature below 70^0C.

Following filtration, enzymatic hydrolyzate and filter cake are obtained. The clear solution of hydrolyzate goes through the storage tank to a vacuum evaporator. The

filter cake is returned to reactor where it is diluted with water, and the heterogeneous mixture is slowly dosed into a hot solution of sodium dichromate and sulphuric acid in a reactor for producing tanning salt. The process flow diagram is shown in Dwg.1 of Annex 1.

3.2. Commercial applications

3.2.1. Agriculture

Both gelatable protein and protein hydrolyzate have positive effect on the growth of plants when applied as fertilizer. The crop yield is comparable with those obtained using inorganic fertilizers but with a significantly high value as foodstuff in view of the low nitrate content which is 20 times less. Besides, organic fertilizer improves the soil quality unlike the inorganic ones. These do not get leached by rain. Another possible area of application is in the manufacture of sowing tapes, which are used to hold specially treated seeds firmly at optimum distance. The organic nitrogen present in the biodegradable tapes is slowly liberated. It acts as a fertilizer and creates a favourable soil micro climate for growth of sprouts.

3.2.2. Building industry

Protein hydrolyzate is a prospective raw material for the production of some additives and auxiliary chemical agents for the building industry. It could be used as an intensifying agent to facilitate the grinding of cement. Protein hydrolyzate is also used as a key ingredient in materials for surface treatment and protection of buildings against pollution. The easiest application is in the production of gypsum plasterboard partitions. Another promising field of application is in the manufacture of prefabricated powdered materials especially for surface finish.

3.2.3. Plastics, resin and rubber industry

Gelatable protein has a positive effect on the antislip properties of flooring and fire surfaces. Applying powdered gelatable protein to the surface increases the friction coefficiency of PVC floorings. The stabilizing effect of powdered gelatable protein and protein hydrolyzate on PVC posters can be also a point of interest. Water solution of protein hydrolyzate can be used as the environment-friendly precipitator of synthetic rubber emulsions. Preliminary results show that an addition of 1% to 5% of 50% hydrolyzate to the adhesive compound considerably increases its bond strength and reduces the content of free formaldehyde in urea and phenol formaldehyde resin. Nevertheless it does not apply in a general way. The effect has to be verified on an actual case-to-case basis.

3.2.4. Processing of filter cakes (chrome sludge)

The filter cakes i.e. chrome sludge can be used in the production of basic chromium sulphate by redox method from solutions of dichromate. Generally, organic reducing agents like molasses, glucose & starch and inorganic reducing agents like sodium thio-sulphate & bisulphite liquor are used for reduction of dichromate. A part of this reducing agent can be replaced by this filter cake. The reaction is exothermic but does

not reach the level experienced with reduction performed with a raw sugar solution so that in this respect it can be well kept under control. However, major difficulties arise when the content of fats or soaps in chrome sludge is higher, when the burning of organic matter under reaction mixture threatens to boil up and thus cause major economic loss.

4. INITIATIVES TAKEN BY UNIDO

Prof. Karel Kolomaznik, of BRNO University, Czech Republic was engaged by UNIDO to demonstrate the technology on enzymatic digestion of chrome shavings. The expert conducted semi-industrial scale trials to produce by-products namely, gelatable protein, protein hydrolyzate and filter cake. The equipment used for the trials, chemicals, process description, and analytical results of products are explained in detail in the following sections. The trials were carried out with the close cooperation of RePO.

5. EQUIPMENT

The following equipment were required for the semi-industrial scale trials on enzymatic digestion of chrome shavings.

1. Reactor with stirrer and heating facility
2. Filter – Gravity filter
3. Evaporator
4. Spray drier

5.1. Reactor

A reactor in the chemical engineering pilot plant at Central Leather Research Institute (CLRI), Adyar, Chennai was used for the digestion of chrome shavings. The reactor is a double jacketed, glass-lined vessel of 250 l capacity. The reactor mixture is indirectly heated by steam. The temperature of the reaction mixture was controlled manually during the operation. The reactor has the following features:

- Anchor type glass lined stirrer driven by 2.2 kW motor
- RPM of the stirrer is 60
- An opening of 150mm dia for feeding chemicals
- Thermowell for inserting thermometer
- Two numbers of sight glass
- Vertical column condenser
- One dummy hole for any other purpose which is closed during the trials
- A valve at the bottom of the reactor to unload the reaction mixture
- Steam inlet and outlet at the steam chamber

Though the vertical column condenser was not directly useful, it helped in condensation of amines evaporated from the mixture, as the height of the column is high enough for natural condensation. A sectional view of the reactor is shown in Dwg.2 of Annex 1.

5.2. Filter

Bag type filtration which uses gravity force was adopted. The specifications of the filter cloth used are as follows:

Name: IFP-1/135 MS Polyester fabric
Manufacturer: Madura Coats India Ltd
Pore size: 25 micron
Capacity: 10 micron solids retention in solution of 5% solid content

The arrangement is explained in Dwg. 3 of Annex 1. For one batch of trial, two filters were required.

5.3. Evaporator

A thin film evaporator in the chemical engineering laboratory of Indian Institute of Technology (IIT) Madras was used. A schematic diagram of the drier is given in Dwg. 4 of Annex 1. Evaporation of the process liquor is done by heating the liquid while falling as thin film and by creating vacuum evaporation. The flow of the liquid which can be read on a flow meter is regulated by a motorized valve. Generally a flow rate of 20 l per hour was found appropriate. Calculation of heat transfer coefficient can be made from the formula in Annex 5.

5.4. Spray drier

A spray drier in the chemical engineering laboratory in IIT was used to obtain spray dried powder of the product. The optimum flow rate of protein solution to the spray drier was 5 kg/hour.

The optimum flow rate of protein solution to the spray drier was evaluated using the heat balance equation as follows:

$$c_p \rho V \Delta t = (s.H)_{ev} m_s \qquad (1)$$

where

c_p	specific capacity of hot air, 1.84 kJ/kg/K (Refer Annex 5)
ρ	density of hot air, 0.81 kg/m (Refer Annex 5)
V	volume flow of air at the outlet of spray drier, 50 m^3/s
Δt	temperature difference between temperature inlet and exhaust air
m_s	steam production

Total mass balance $P = S + m_s$ (2)
Solid mass balance $P.a_{S,P} = S$ (3)

P - input of a concentrated protein solution (kg/s)
$a_{S,P}$ – mass fraction of dry matter in P

Substituting S from (3) into (2) we receive:

$$m_s = P(1 - a_{S,P}) \quad (4)$$

Finally using (4) in (1) and we get:

$$P = \frac{c_p \rho V \Delta t}{(sH)_{ev}(1 - a_{S,P})} \quad (5)$$

Substituting the values, we receive:

$$P = \frac{0.81\text{x}1.84\text{x}50\text{x}3600\text{x}120\text{x}10^3}{3600\text{x}2.25\text{x}10^6\,\text{x}(1-0.2)} = 4.97 kg/h$$

Hence the capacity or the optimum flow rate may be taken as 5 kg /h.

6. CHEMICALS

The requirement of chemicals for the enzymatic digestion of chrome shavings are given in table 2.

Table 2: Chemical requirement for enzymatic digestion of chrome shavings

S. No.	Name of chemical	Percentage on weight of chrome shavings	Specification
1.	Magnesium oxide	2%	Particle size: 200 mesh, Purity 75-80%,
2.	Isopropyl amine	3%	Purity: 75%
3.	n-butyl amine	3%	Purity: 100%
4.	Alcalase (enzyme)	0.03%	Proteolytic activity: 2.77 AU/g, Total viable count: <1/g, Viscosity at 25^0C: <11,
5.	Potassium hydroxide	3%	in pellets
6.	Ortho-phosphoric acid	2%	85% Purity

The chemicals used for the laboratory scale trials are given in table 3.

Table 3: Chemicals used in the laboratory scale trials

S. No.	Name of chemical	Quantity	Specification
1.	Sulphuric acid N/10	500 ml	Analar Grade
2.	Sodium dichromate	1 kg	$Na_2Cr_2O_7.2H_2O$
3.	Gluteraldehyde	100 ml	
4.	Sodium carbonate	1 kg	Industrial grade
5.	Sodium formate	1 kg	Industrial grade
6.	Common salt	2 kg	

7. PROCESS DESCRIPTION

The digestion of chrome shavings is done in two stages. In the first stage, the chrome shavings are digested for three to five hours in alkaline condition and at a temperature of 70^0C to produce gelatable protein. This stage is called denaturation. After digestion the reaction mixture is filtered through a filter cloth. The filtrate obtained is called gelatable protein. This product contains hydrolyzate of protein with high molecular weight. The filter cake obtained from this first stage digestion is further digested using enzymes and at a temperature of 70^0C for two hours. The reaction mixture is filtered again and the filtrate obtained is protein hydrolyzate. The second stage digestion is called enzymatic hydrolysis. The enzymatic hydrolyzate contains protein of lower molecular weight than the first stage digestion.

The following four trials of enzymatic digestion were done.

1. Production of gelatable protein, protein hydrolyzate and filter cake using isopropyl amine
2. Production of NPK fertilizer and filter cake using ortho-phosporic acid and potassium hydroxide
3. Production of gelatable protein, protein hydrolyzate and filter cake using n-butyl amine
4. Repetition of trial-1

In the first three trials, goat skin shavings were used and in the 4^{th} trial, cow hide shavings were used.

7.1. Trial 1 - Production of gelatable protein, protein hydrolyzate and filter cake using isopropyl amine

The following procedure was followed.

- 600 g of Magnesium oxide dissolved in 5 l of water in a bucket
- 100 l of water poured into the reactor
- MgO suspension was added with stirring on
- Stirring continued for 15 min
- 855 g of isopropyl amine dissolved in 5 l of water was added
- 30 kg chrome shavings was charged

- Water to make up total volume of 150 l was added
- After 30 min of stirring, pH was 12. An excess of 341 g of isopropyl amine was added
- Stirring was continued for one hour and the mixture left overnight

Next day stirring was done for 15 minutes and heating started. The temperature, pH and other observations made are given in table 4.

Table 4: Observations made during trial 1

Time in hours	Temperature in ^{0}C	pH	Remarks
1030	30	12	Start heating
1045	45	-	
1130	70	-	
1200	72	9.95	Slight sticky
1300	69	9.35	Very slight yellow colour
1400	68	9.40	Tested for jelly
1500	68	9.35	Jelly test positive, reaction complete

End point of digestion:

- Check viscosity (the filtrate should be viscous)
- Colour of filtrate slight yellow
- Filtrate to be sticky
- Jelly test (the filtrate becomes jelly after chilling for about ½ hour)

After completion of reaction, the mixture was drained directly into two numbers of bag filters for gravity filtration. The filtration continued overnight. The gelatable protein (filtrate) was weighed and sample collected for analysis. 0.5% of preservative (LUNACID) based on TCMTB was added to the gelatable protein.

Weight of gelatable protein (GP-1): 108 kg
Weight of filter cake: 54 kg

The filter cake was again taken up for further processing. 200% of water based on initial weight of chrome shavings was added. Filter cake was added into the reactor with stirring. After reaching 70^{0}C (30 min in this trial), stirring was continued for 30 min and the temperature maintained at 70^{0}C. The pH of the mixture was 9.0 and hence addition of amine was not required. If the pH was less, it should have been adjusted by adding isopropyl amine. 0.03% enzyme was added and reaction continued for one hour. The reaction mixture was checked visually and it was observed that the size of solid particles in the reaction mixture was smaller than the applied chrome shavings. The filtrate was slightly yellow in colour, which showed the completion of the reaction.

After completion of reaction, the reaction mixture was filtered in two numbers of bag filters. Filtration was continued overnight. Next day, the protein hydrolyzate (filtrate) and filter cake were weighed.

Weight of protein hydrolyzate (PH-1):	81 kg
Weight of filter cake (FK-1):	32 kg

7.2. Concentration of gelatable protein and protein hydrolyzate

The gelatable protein and protein hydrolyzate were concentrated in a thin film evaporator. The solid concentration was increased to 20% from initial 5%. The protein hydrolyzate was concentrated to 64% solid content. The evaporation was done at 90^0C. The input flow rate was kept at 20 l per hour. Evaporation of the gelatable protein was done in two cycles. Evaporation of protein hydrolyzate was done in 3 cycles.

The solid content in the product was derived using the following equation.

$$V_{GP-1} \times S_{GP-1} = C_{GP-1} \times S_{C,GP-1}$$

V_{GP-1}	Weight of input gelatable protein
S_{GP-1}	Solid content of input gelatable protein
C_{GP-1}	Weight of concentrated GP-1
$S_{C,GP-1}$	Solid content of concentrated GP-1

A small quantity of concentrated gelatable protein was spray dried. About 500 g of spray dried powder was obtained. However further spray drying could not be continued, as the product began sticking to the wall of the dryer.

7.3. Trial 2 - Production of NPK fertilizer

Quantity of chrome shavings: 30 kg

- Dissolve 0.678 kg KOH in 10 l of water and 0.683 kg ortho-phosphoric acid solution in 10 l
- Prepare mixture of KOH solution and phosphoric acid solution.
- Prepare suspension of 0.3 kg MgO in 10 l of water
- Add 120 l of water into the reactor
- Add suspension of MgO during stirring
- Add mixture of KOH and phosphoric acid
- Start heating
- Add chrome shavings into the reactor while stirring

The observations on temperature, pH and other observations are given in table 5.

Table 5: Observations made during I stage digestion of trial-2

Time in hours	Temperature in ^{0}C	pH	Remarks
1050	31	-	Start heating
1105	56	7.5	+ 30 g KOH
1125	65	7.5	+ 30 g KOH
1135	68	7.5	+ 60 g KOH
1150	70	7.5	+ 60 g KOH
1200	70	8.0	+ 80 g KOH
1215	70	-	+ 50 g KOH
1300	68	8.5	+ 15 g enzyme ALKALASE
1430	70	8.0	+ 80 g KOH
1500	69	8.0	+ 200 g MgO
1600	69	7.8	Stirring and heating continued for one hour

The total input to the system was as follows:

Chrome shavings: 30 kg
Potassium hydroxide: 1.068 kg
Phosphoric acid: 0.683 kg
Water: 155 l

After completion of reaction, the mixture was filtered and the filtration was continued overnight. After completion of filtration, the products were weighed.

Weight of fertilizer (NPK1): 134 kg
Weight of filter cake: 41 kg

The filter cake was loaded into the reactor for second stage enzymatic digestion. The observations are given in table 6.

Input: Filter cake: 41 kg, Water: 60 l

Table 6: Observations made during II stage digestion of trial-2

Time in hours	Temperature in ^{0}C	pH	Remarks
1030	32	9.0	Start heating and stirring
1045	70	-	
1100	71	-	Add 15 g ALKALASE (enzyme) i.e. 0.03% on weight of chrome shavings)

1200	70	9.0	-
1300	-	-	Unloaded

Filtering of the reactor mixture was done in a bag filter. Filtration was continued through the tight.

Weight of fertilizer (NPK2): 58 kg
Weight of filter cake (FK-2): 26 kg

NPK fertilizer-1 and NPK fertilizer-2 were mixed together.

The combined NPK fertilizer was concentrated to 20% solid content using a thin film evaporator.

7.4. Trial 3 - Production of gelatable protein and protein hydrolyzate using n-butyl amine

The third trial was similar to the first trial except that isopropyl amine was replaced with n-butyl amine. The input to the system for alkaline digestion was as follows:

Chrome shavings: 30 kg
Water: 150 l
Magnesium oxide: 0.6 kg
n-butyl amine: 0.9 kg

The ingredients were soaked overnight and digested for 4 ½ hours at 70^0C. The products obtained were as follows:

Weight of gelatable protein (GP-2): 120 kg
Weight of filter cake: 51 kg

The filter cake was loaded into the reactor containing 60 l of water, i.e. 200% on initial weight of chrome shavings, and heated to 70^0C. After reaching a temperature of 70^0C, 15 g of enzyme ALKALASE, i.e. 0.03% on initial weight of chrome shavings, was added and digestion continued for 2 hours. Filtration of the mixture was done overnight. The following products were obtained after filtration.

Weight of protein hydrolyzate (PH-2): 70 kg
Weight of filter cake (FK-3): 32 kg

The gelatable protein was concentrated to 30% solid content and protein hydrolyzate was concentrated to 50% solid content using a thin film evaporator.

7.5. Trial 4 - Production of gelatable protein and protein hydrolyzate using isopropyl amine (repetition of trial-1)

In this trial, wetblue shavings from cow hide was used for the digestion. Similar to the first trial, 30 kg of shavings was taken for process and the following chemicals were used.

Magnesium oxide:	0.6 kg
Isopropyl amine:	1.2 kg
Water:	150 l

Magnesium oxide was dissolved in 10 l of water and added to the reactor containing 120 l of water while stirring. Isopropyl amine was diluted with 10 l of water and added to the reactor. The total volume of water was adjusted to 150 l. After stirring for 10 minutes, the pH was 12. Chrome shavings was added to the reactor. Stirring was continued for one hour and the mixture left overnight. The denaturation was done for 5 hours at 70^{o}C. The pH of the reaction mixture was 10 at the beginning and at the end 9.5. After overnight filtration, the following products were obtained.

Weight of gelatable protein (GP-3):	106 kg
Weight of filter cake:	65.5 kg

The filter cake was loaded again to the reactor for enzymatic digestion with 60 l of water and 15 g of enzyme ALKALASE. The digestion took two hours and following filtration, hydrolyzate and filter cake were obtained as detailed below:

Weight of protein hydrolyzate (PH-3):	58 kg
Weight of filter cake (FK-4):	39 kg

The gelatable protein and protein hydrolyzate were concentrated to 30% and 50% solid contents respectively.

Analytical data of the gelatable protein, protein hydrolyzate and NPK fertilizer are given in Annex 2.

The typical amino acid composition of an enzymatic hydrolyzate is given in table 7.

Table 7: Amino acid composition of enzymatic hydrolyzate

Amino acid	%
Aspartic acid	4.6
Hydroxyproline	9.4
Threonine	2.0
Isoleucine	1.1
Leucine	2.2
Phenylalanine	1.1
Serine	3.1
Glutamic acid	7.6

Proline	12.2
Glycine	33.2
Alanine	12.0
Methoionine	1.0
Histidine	0.3
Hydroxylisine	0.8
Lysine	2.5
Arginine	5.2
Valine	1.7

7.6. Recycling of filter cake

7.6.1. Preparation of tanning liquor

A laboratory trial was done to produce basic chromium sulphate using filter cake obtained in the first trial.

The following materials were used in this test:

Sodium dichromate:	110.2 g
Sulphuric acid:	154 g (= 84 ml)
Filter cake:	200 g dissolved in 200 ml of water

Sodium dichromate was weighed into a 2 l conical flask and 84 ml of conc. sulphuric acid added to it very slowly. The mixture was heated to 60^{o}C inside a fume chamber. The filter cake suspension was added very slowly and carefully into the conical flask with frequent stirring. The filter cake was added for a period of 20 minutes. Liberation of gases was observed during addition of filter cake suspension. After addition of filter cake, the reaction mixture was heated to 70 - 80^{o}C for about 10 minutes with frequent stirring. Excess dichromate was reduced using sugar by adding slowly till the colour changed to green. 6.6 g of sugar was used. The completion of reduction of dichromate into trivalent chromium was checked in a test tube by adding potassium iodide solution and starch indicator (The appearance of blue colour indicates presence of hexavalent chromium). The pH of the reaction mixture was 1.35. The reaction mixture was allowed to cool.

The volume of chrome liquor was 590 ml and the chrome content (Cr_2O_3) was 67 g/l. The basicity was 20%. 11 g of sodium carbonate was added to increase the basicity to 33%. The analytical data of the recovered chrome liquor is given in Annex 2.

Stoichiometric calculations on the quantity of ingredients namely, sulphuric acid, filter cake and sodium dichromate are made based on the following equations. Molecular weight of the relevant chemicals is given in Annex 5.

$$2\ C_3H_5NO + 5\ Na_2Cr_2O_7 + 20\ H_2SO_4 = 6\ CO_2 + N_2 + 25\ H_2O + 5\ Cr_2(SO_4)_3 + 5\ Na_2SO_4$$

The filter cake contributed 1.411 g of Cr_2O_3 which is about 4% of total chromium content in tanning liquor.

The reduction capacity of filter cake is calculated as follows:

$8\ Na_2Cr_2O_7 + 32\ H_2SO_4 + C_{12}H_{22}O_{11} = 8\ Na_2SO_4 + 8\ Cr_2(SO_4)_3 + 43\ H_2O + 12\ CO_2$

Molecular weight of $Na_2Cr_2O_7$ is 352.043 and sucrose is 343.5053 (Refer Annex 5).

$$6.6\ g \text{ sugar eliminates} \qquad \frac{6.6x8x352.043}{343.5052} = 54.11\ g \text{ dichromate}$$

The consumption of dichromate for oxidation of protein in the filtrate cake is

$$110.2201 - 54.112 = 56.089\ g\ \ Na_2Cr_2O_7\ .\ 2\ H_2O$$

Therefore, quantity of protein used for reduction of dichromate is

$$\frac{2x71.079x56.089}{5x352.043} = 4.53\ g\ \ protein.$$

Reduction capacity of filter cake is = 280 g $Na_2Cr_2O\ .\ H_2O$ / kg FK*
= 2.3 kg $Na_2Cr_2O_7$/kg FK**

*moisture = 88 %, solid 12 %
**free moisture base

7.6.2. Trial on chrome tanning using the tanning liquor produced

A pickled sheep skin was tanned using the tanning liquor produced from the above trial. The pickled skin weighed 1,030 g. The pelt weight was obtained by adding 30% to the pickled weight. Tanning was done applying chrome liquor prepared using filter cake. The process adopted is described in table 8.

Pelt weight = pickle weight + 30% = 1,340 g

Table 8: Chrome process using the tanning liquor produced using filter cake

Operation	Chemicals / water	% on pelt weight	Quantity	Run time	Check / remarks
	Water	80	1,075 ml		
	Salt	8	11 g	10 min.	8^0 Bé
Load skin				15 min.	pH 2.8 – 3.0
Drain half float					
	Recovered	1% Cr_2O_3	200 ml	45 min.	

	chrome liquor				
	Recovered chrome liquor	1% Cr_2O_3	200 ml	100 min.	Penetration
	Water		300 ml	10 min.	
	Sodium formate	1	13.4 g	15 min.	
	Sodium bicarbonate (dissolve in 100 ml water)	1	13.4 g	4 x 10 min + 60 min.	pH 3.8 – 4.0

The wetblue leather produced was kept for a day for ageing. Next day, the leather was tested for shrinkage temperature and chrome content and the spent chrome liquor was tested for chrome content. The following results were obtained.

Chrome uptake by the skin: 81%
Chrome content in the wetblue: 3.93% Cr_2O_3 on dry weight basis
Shrinkage temperature of the wetblue: 118^0C

As may be seen from the results, the wetblue leather has the required specifications and characteristics.

8. ANALYTICAL TESTS CONDUCTED

The various analyses carried out on the products of hydrolysis are given in table 9. Nitrogen content was tested by TKN method.

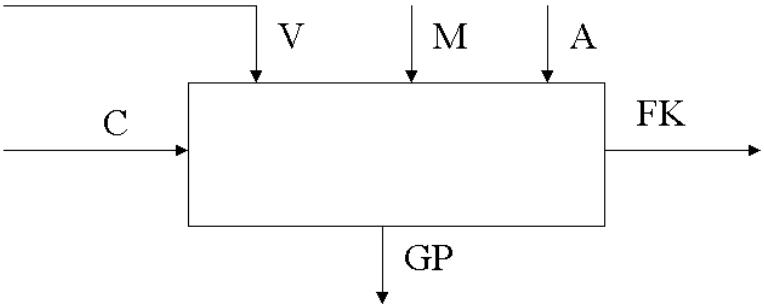
Table 9: Analyses carried out for the products of hydrolysis

Product	Analytical tests
Chrome shavings	Moisture content, total nitrogen, ash content and chrome content
Gelatable protein	Solid content, ash, nitrogen, chrome content, volatile solids
Protein hydrolyzate	Solid content, ash, nitrogen, chrome content and volatile solids
Filter cake	Moisture, ash, nitrogen and chrome content, volatile solids and magnesium in one batch
NPK fertilizer	Solid content, ash, nitrogen, potassium and phosphorus
Recovered chrome liquor	Chrome content, basicity and pH
Spent chrome liquor	Chrome content
Wetblue	Chrome content and shrinkage temperature

The analytical results of chrome shavings and the products obtained in the trials are given in Annex 2.

9. RESULTS – MATERIAL BALANCE ANALYSIS

9.1. Preliminary calculations



C – chrome shavings	[kg]
V – water	[kg]
M – magnesium oxide	[kg]
A - amine	[kg]
FK – filtrate cake	[kg]
GP – gelatable protein. (Water solution)	[kg]

Total mass balance

$$C + V + M + A = FK + GP \tag{1}$$

Mass balance of solid phase

$$C.a_{S,C} + M = FKa_{S,FK} + GPa_{S,GP} \tag{2}$$

$a_{S,C}$	mass fraction solid in C (chrome shaving)
$a_{S,FK}$	mass fraction solid in FK (filtrate cake)
$a_{S,GP}$	mass fraction solid in GP (gelatable protein)

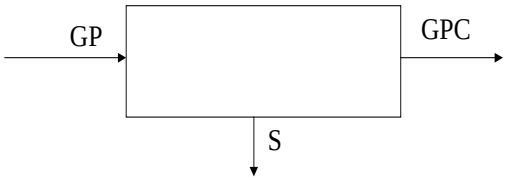
from (1) we receive for FK

$$FK = C + V + M + A - GP \tag{3}$$

Putting (3) into (2) and after arrangement we get

$$GP = \frac{C\left(a_{S,C} - a_{S,FK}\right) - \left(V + A\right)a_{S,FK} + M\left(1 - a_{S,FK}\right)}{a_{S,GP} - a_{S,FK}} \tag{4}$$

Concentration of GP



GPC	Gelatable protein concentrate	[kg]
S	Steam	[kg]
$a_{S,GPC}$	Mass fraction solid in gelatable protein concentrate	[1]

Total balance

$$GP = GPC + S \tag{5}$$

Balance of solid

$$GPa_{S,GP} = GPCa_{S,GPC} \tag{6}$$

from (6) we obtain

$$GPC = \frac{GP.a_{S,GP}}{a_{S,GPC}} \tag{7}$$

9.2. Trial 1 Production of gelatable protein and protein hydrolyzate

Total balance

Input		Output	
Chrome shavings	30 kg	Gelatable protein	108 kg
Magnesium oxide	0.6 kg	Protein hydrolyzate	81 kg
Isopropyl amine	1.196 kg	Filter cake	32 kg
Water	210 l		
Total	241.796 kg	Total	221 kg

Loss due to evaporation: 20.796 kg (8.6%)

Nitrogen balance

Input		Output	
Chrome shavings	1.081 kg	Gelatable protein	0.896 kg
Iso-propyl amine	0.288 kg	Protein hydrolyzate	0.737 kg
		Filter cake	0.101 kg
Total	1.369 kg	Total	1.734 kg

Solid balance

Input		Output	
Chrome shavings	10.851 kg	Gelatable protein	5.368 kg
Magnesium oxide	0.6 kg	Protein hydrolyzate	4.633 kg
		Filter cake	3.821 kg
Total	11.451 kg	Total	13.822 kg

9.3. Trial 2 Production of NPK fertilizer

Total balance

Input		Output	
Chrome shavings	30 kg	NPK fertilizer-1	134 kg
Ortho phosphoric acid	0.683 kg	NPK fertilizer-2	58 kg
Potassium hydroxide	1.068 kg	Filter cake	26 kg
Magnesium oxide	0.500 kg		
Water	215 l		
	247.251 kg	Total	218 kg

Loss due to evaporation: 29.251 kg (12%)

Solid balance

Input		Output	
Chrome shavings	10.851 kg	NPK fertilizer-1	6.553 kg
Ortho phosphoric acid	0.580 kg	NPK fertilizer-2	1.891 kg
Potassium hydroxide	1.068 kg	Filter cake	5.088 kg
Magnesium oxide	0.500 kg		
	12.999 kg	Total	13.532 kg

Nitrogen balance

Input		Output	
Chrome shavings	1.081 kg	NPK fertilizer-1	0.777
		NPK fertilizer-2	0.499
		Filter cake	0.031
Total	1.081 kg	Total	1.307 kg

9.4. Trial 3 Production of gelatable protein and protein hydrolyzate using n-butyl amine

Total balance

Input		Output	
Chrome shavings	30 kg	Gelatable protein	120 kg
Magnesium oxide	0.6 kg	Protein hydrolyzate	70 kg
n-butyl amine	0.9 kg	Filter cake	32 kg
Water	210 l		
Total	241.5 kg	Total	222 kg

Loss due to evaporation: 19.5 kg (8%)

Nitrogen balance

Input		Output	
Chrome shavings	1.081 kg	Gelatable protein	0.596 kg
n-butyl amine	0.172 kg	Protein hydrolyzate	0.218 kg
		Filter cake	0.282 kg
Total	1.253 kg	Total	1.096 kg

Solid balance

Input		Output	
Chrome shavings	10.851 kg	Gelatable protein	4.188 kg
Magnesium oxide	0.6 kg	Protein hydrolyzate	3.304 kg
		Filter cake	5.590 kg
Total	11.451 kg	Total	13.082 kg

10. EQUIPMENT RECOMMENDED FOR INDUSTRIAL SCALE PLANT

10.1. Reactor

A reactor of the type used in the trials and with a capacity to handle a load of 3 tonnes is recommended for industrial scale operation.

10.2. Filter

Bag filters used in the trials cannot be used in industrial scale plants. In the industrial scale plant use of a vacuum filter or vacuum press filter is recommended. The capacity of filter is calculated as follows:

In the trials carried out, after the reaction was completed, the heterogeneous blend was filtered using bag filters. 20 liters of pure filtrate was obtained in 2 hours. The

volume of filtrate obtained in 2 hours enables us to estimate the specific resistance of a filtrate cake (β). The specific resistance of a filtrate cake (β) is an important constant required in the calculations of the filter area in industrial scale plant. A sack filter of size: diameter d = 52 cm, and height h = 40 cm, gives a filter area (S)

$$S = \pi.d\left(\frac{d}{4} + h\right) = \pi.0.5\left(\frac{0.52}{4} + 0.2\right) = 0.866\, m^2 \cong 0.87\, m^2 \qquad (1)$$

The simplest integrated filter equation under the constant of a pressure difference is:

$$K.\tau = \frac{V_F{}^2}{2} \qquad (2)$$

where

V_F	volume of filtrate [m^3] obtained during time τ [s]
K	constant of filtration

$$K = \frac{V_F{}^2}{2\tau} = \frac{0.02^2}{2\text{x}3600} = 5.56\text{x}10^{-8}\ m^6 / s$$

The filter constant depends on the specific resistance of a filtrate cake:

$$K = \frac{\Delta p.S^2}{\mu\beta} \qquad (3)$$

where

Δp	pressure difference [Pa]
μ	dynamic viscosity of filtrate [Pas], (2cP = $2\text{x}10^{-3}$ Pas – estimated)
β	specific resistance of filter cake [m^{-2}]

from (3) for β is derived as

$$\beta = \frac{\Delta p.S^2}{\mu.K} \qquad (4)$$

The pressure difference (Δp) is

$$\Delta p = \rho.g.\Delta.h \qquad (5)$$

where

ρ	density of a reaction mixture 1,000 kg / m^3 (estimated)
g	gravitation acceleration 9.81 m / s^2

Δh average height of a reaction mixture, 0.15 m

Hence, $\Delta p = 1000 \times 9.81 \times 0.15 = 1.47$ k.Pa

and $\beta = \frac{1470 \text{x} 0.87^2}{2\text{x}10^{-3} \text{x} 5.56\text{x}10^{-8}} = 1.0006\text{x}10^{13} m^{-2} \cong 10^{13} m^{-2}$

While processing 3 tonne of chrome shavings, 12 m^3 of dilute gelatable protein will be produced. With 2 hours for filtration, the filter area is calculated as follows:

$$K = \frac{V_F^{\ 2}}{2\tau} = \frac{12^2}{2\text{x}3600} = 0.02\ m^6 / s$$

from (4) $S = \left(\frac{\beta.\mu.K}{\Delta p} \right)^{0.5} = \sqrt{\frac{10^{13} \text{x} 2\text{x}10^{-3} \text{x} 0.02}{2\text{x}10^5}} = 44.72\ m^2$

Hence the filter area required for a vacuum filter is about 45 m^2 while processing 3 tonne of chrome shavings. In view of this, use of a vacuum filter is recommended for this application. The best option is to use a continuous working belt filter or a partial filtrate process.

10.3. Vacuum film evaporation

A three stage evaporator is recommended for evaporation of the gelatable protein and protein hydrolyzate. A typical schematic diagram is given in Dwg. 5 of Annex 1.

10.4. Spray drier

The spray drier recommended for use in the industrial scale plant should be based on jet and not rotary disk. The rotary disk creates fine drops which are not dried completely due to poor heat transfer. Hence it is recommended to use jet which creates fog and not drops. Fog has larger surface area and thus the drying is complete. For efficient spray drying the temperature of exhaust air should be close to ambient temperature. A typical schematic diagram is given in Dwg. 6 of Annex 1.

11. COST OF PRODUCTS AND THEIR MARKET POTENTIAL

A summary of the estimated operational cost and calculation of processing cost are enclosed at Annex 3. From this, it may be seen that the cost will vary according to the equipment and chemicals used. It ranges from Rs. 2.24 to 12.65 per kg for gelatable protein and Rs. 4.05 to 6.34 per kg of protein hydrolyzate. The processing cost per kg of chrome shavings varies from Rs. 2.84 to 10.54.

The feasibility of commercial application of these products in Indian conditions was discussed in a meeting with selected persons – by product manufacturers and

scientists. A copy of the minutes of the meeting may be seen at Annex 4. The main conclusions arrived at were:

a. Application of gelatable protein in building or plywood industry is not in practice at present in India. Its marketability, therefore, has to be specifically verified.
b. The cost of fertilizer was found to be too high for the Indian market at present.

12. CONCLUSION AND FUTURE COURSE OF ACTION

The products obtained from the digestion of chrome shavings have a wide range of industrial applications. The technology is simple and not many process controls are required. This method may offer a solution for utilization of excess chrome shavings, which are often dumped in the open at present and sometimes, even burnt out! The products were displayed and samples given to the industry representatives related to this field.

Commercial benefits of the system should be linked with both the value of the products and the disposal cost of chrome shavings. Equipment required for digestion of chrome shavings by this method and the cost of operation are likely to be high. However when compared with the cost of disposal of the chrome shavings, usable products can be obtained from this waste material.

This technology may be suitable for a cluster of tanneries. There should be proper arrangement with the basic chromium sulphate manufacturers for using up the chrome sludge produced.

Though the products have many industrial applications, market for these products will have to be developed in India & elsewhere in the region.

ACKNOWLEDGEMENT

Contributions of the following individuals / organizations to the successful implementation of the project are gratefully acknowledged.

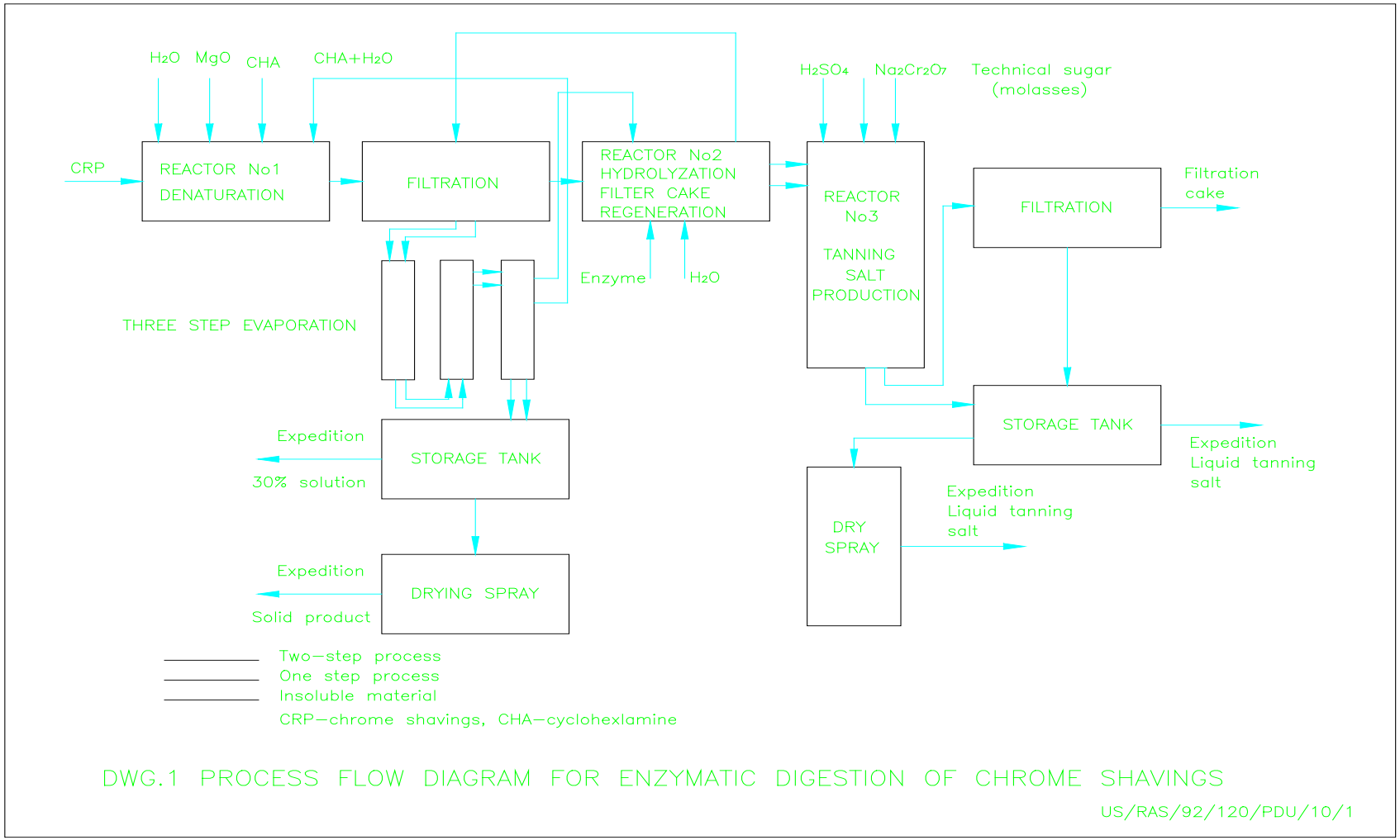
1. Dr. T. Ramasami, Director, Dr. P.G. Rao, Deputy Director and Scientists of Central Leather Research Institute, Chennai.
2. Dr. Krishnaiah and Staff of Chemical Engineering pilot plant of Indian Institute of Technology Madras, Chennai.
3. Dr. Prakash Rao and Dr. Muralidhar Rao, Prakash Feed Mills Pvt. Ltd, Chennai

REFERENCE

Experience in industrial practice of enzymatic dechromation of chrome shavings, K. Kolomaznik, et.al., JALCA, Vol. 94, 1999.

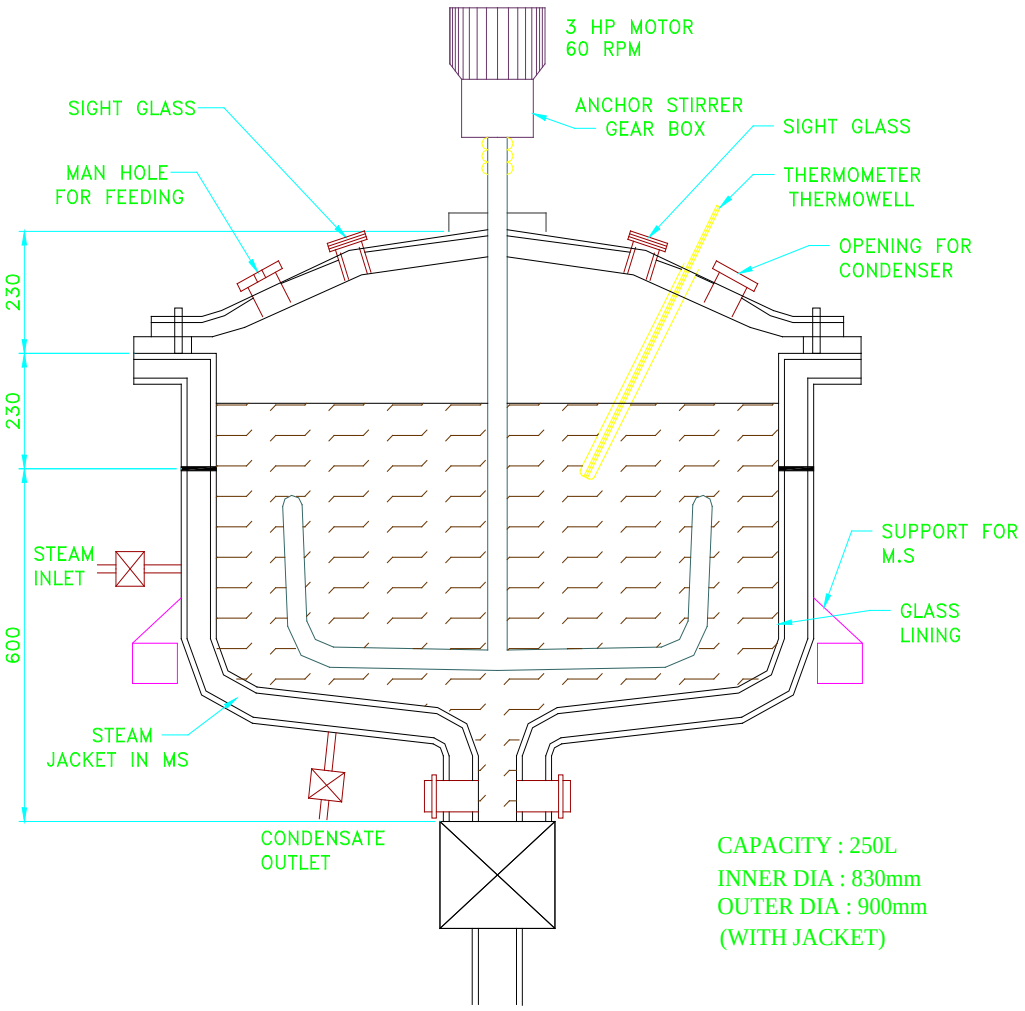
Annex 1

Drawings



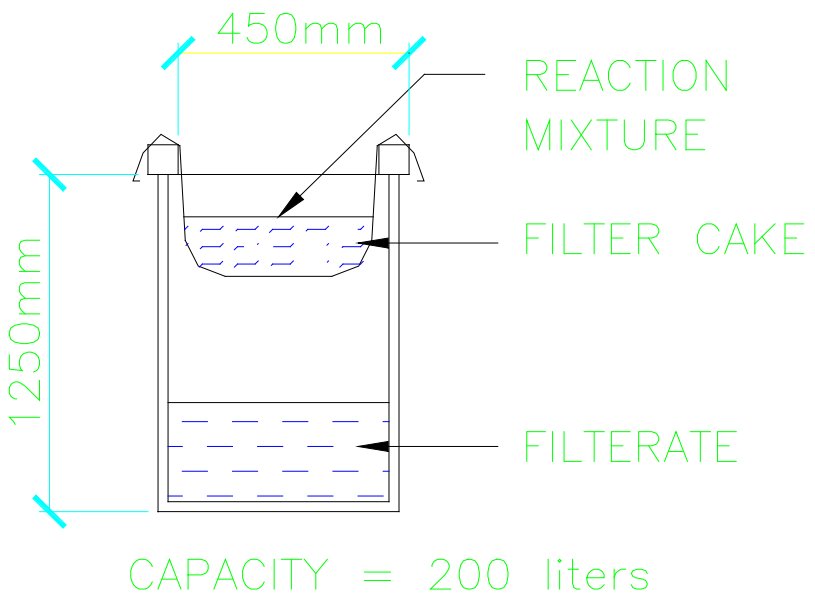
DWG.1 PROCESS FLOW DIAGRAM FOR ENZYMATIC DIGESTION OF CHROME SHAVINGS

US/RAS/92/120/PDU/10/1



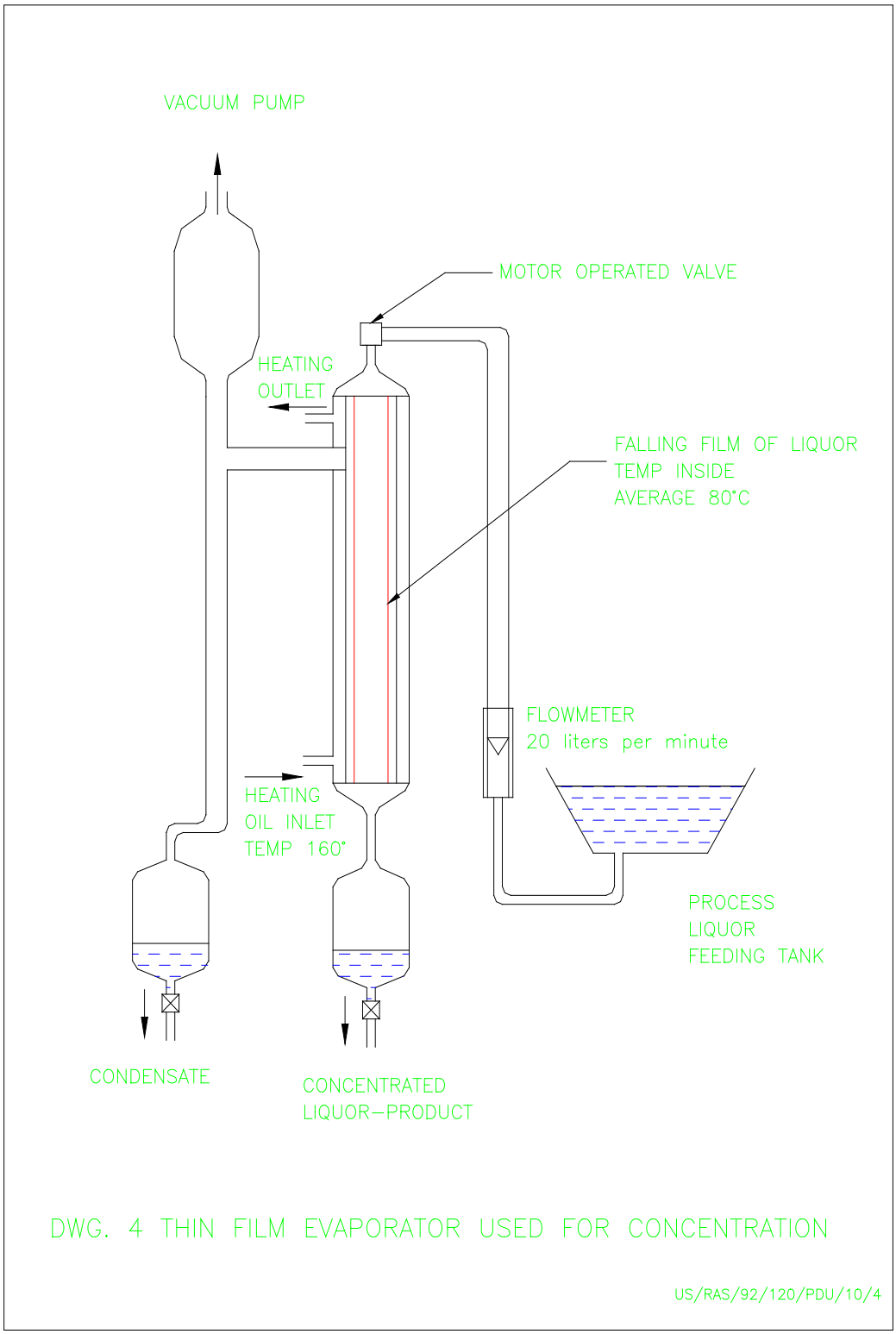
DWG. 2 REACTOR USED FOR DIGESTION OF CHROME SHAVINGS

US/RAS/92/120/PDU/10/2



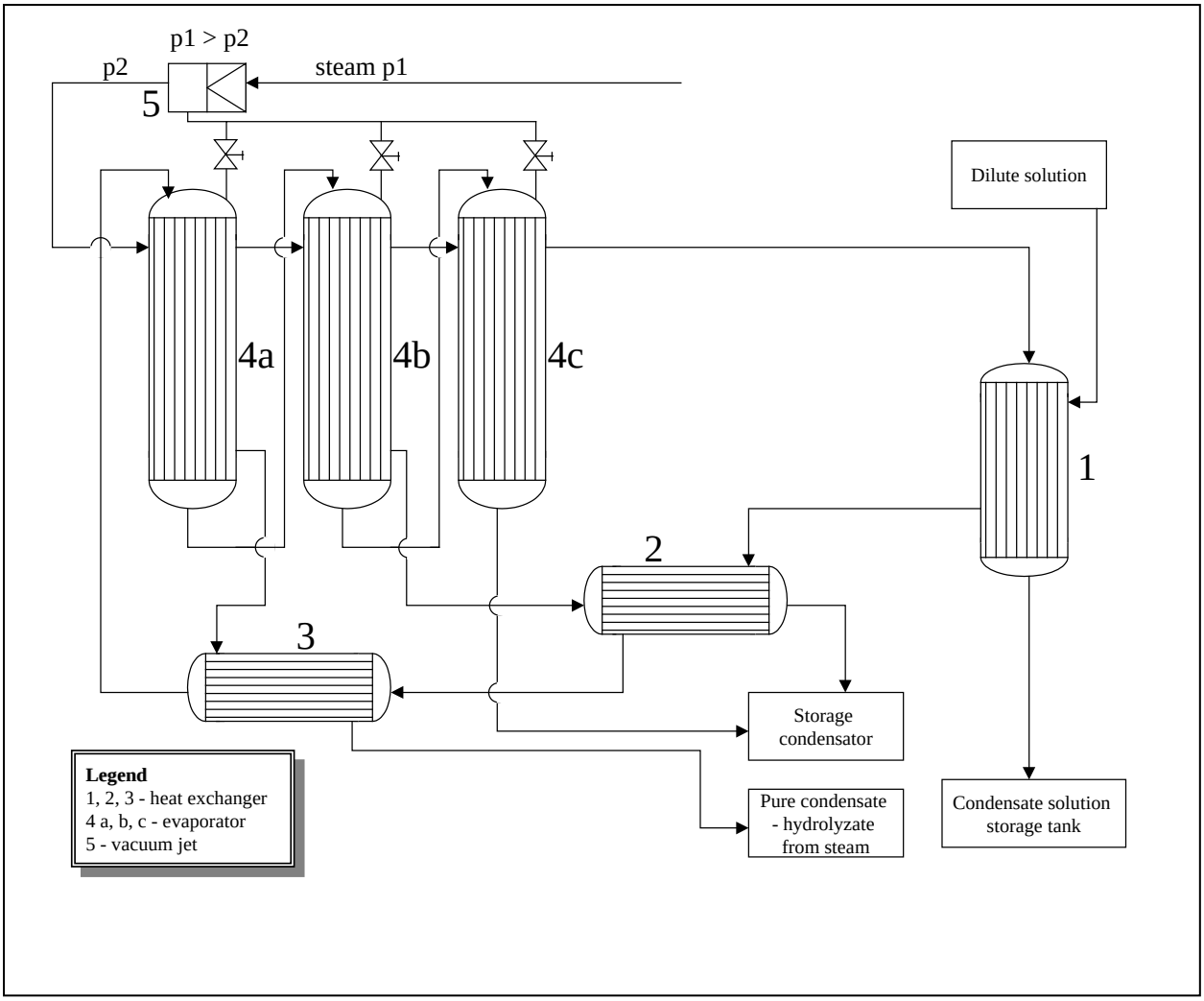
DWG. 3 BAG TYPE FILTER USED FOR FILTRATION

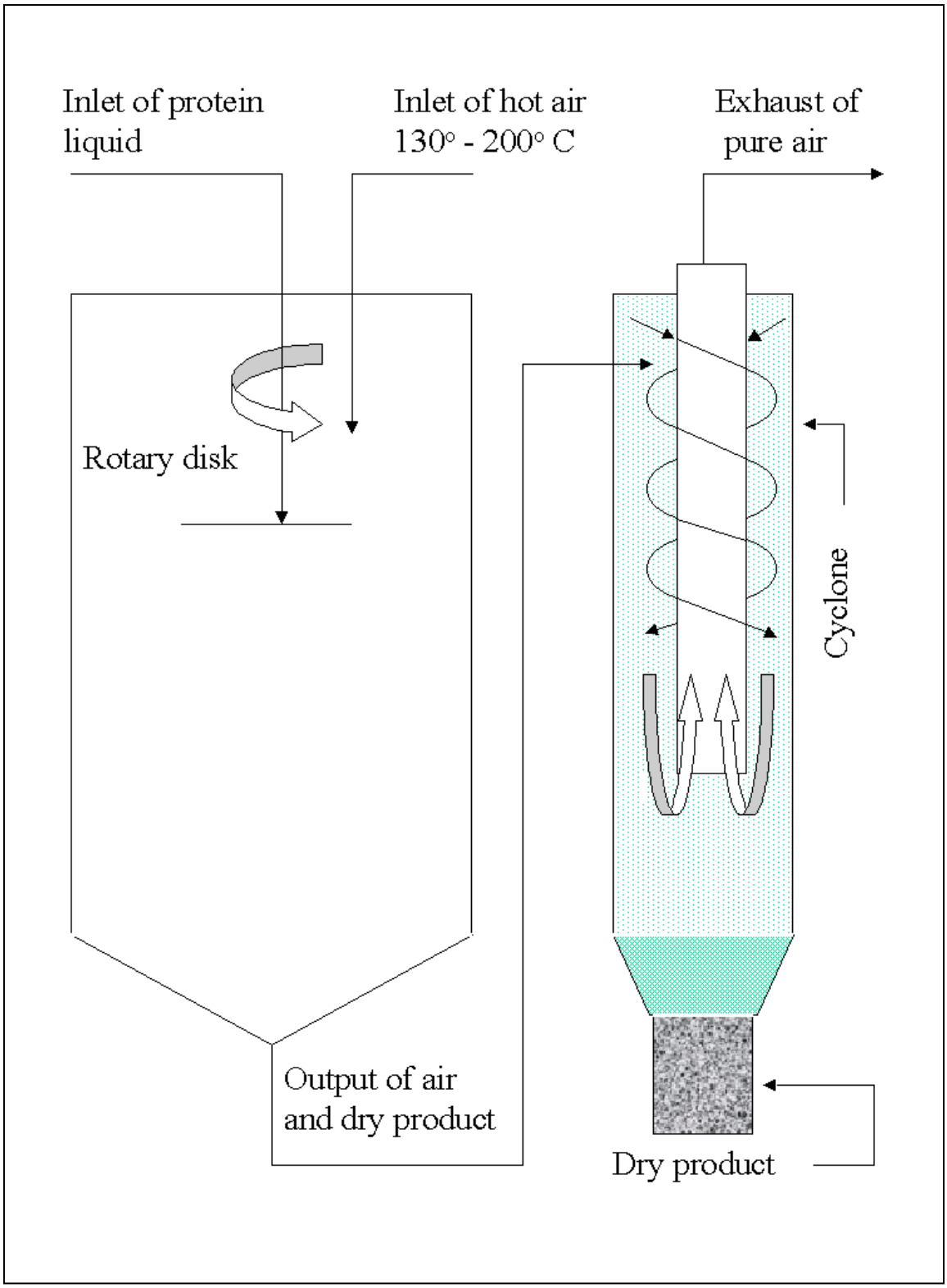
US/RAS/92/120/PDO/10/3



DWG. 4 THIN FILM EVAPORATOR USED FOR CONCENTRATION

US/RAS/92/120/PDU/10/4


p1 > p2
p2
steam p1
5
Dilute solution
4a
4b
4c
1
2
3
Storage condensator
Legend
1, 2, 3 - heat exchanger
4 a, b, c - evaporator
5 - vacuum jet
Pure condensate - hydrolyzate from steam
Condensate solution storage tank


Inlet of protein liquid
Inlet of hot air 130° - 200° C
Exhaust of pure air
Rotary disk
Cyclone
Output of air and dry product
Dry product

Annex-3 Details of processing cost

A. SUMMARY OF PROCESSING COSTS

Items	PRODUCTION COST RS./KG		Cost of processing of chrome shavings Rs/kg	Unit cost (Rs./kg)	% C	REMARKS
	GP	PH				
Magnesium oxide	0.24	0	0.16	8	2	-
n-butyl amine	9.5	0	6.33	211	3	
Water	0.2	0.03	0.14	0.044	500[1] 200[2]	[1]GP [2]PH
Enzyme	0	1.8	0.6	2,000	0.03	
Initial heating	0.30	0.30	0.30	Rs.200/GJ[3]	-	[3] estimated, Rs.150 /GJ in CR
Stirring	0.08	0.08	0.08	Rs.4/kWh	-	-
Heat loss	0.08	0.08	0.08	Rs.200/GJ	-	Non insulated reactor
Heat loss	0.0002	0.0002	0.0002	Rs.200/GJ	-	Insulated reactor
Evaporating[4]	2.25	4.05	2.85	Rs.200/GJ	-	[4] one step evaporator
Evaporating[5]	0.98	1.76	1.24	Rs.200/GJ	-	[5] three steps evaporator
Total	12.65	6.34	10.55	-	-	One step evaporator
	11.38	4.05	8.93 [a]	-	-	[a] three steps evaporator
	11.31	-	8.86 [b]	-	-	[b] insulated reactor
Replacement of n-butyl amine by MgO	3.51	-	4.45	-	6	One step evaporator
	2.24	-	2.84 [c]	-	6	[c]Three steps evaporator

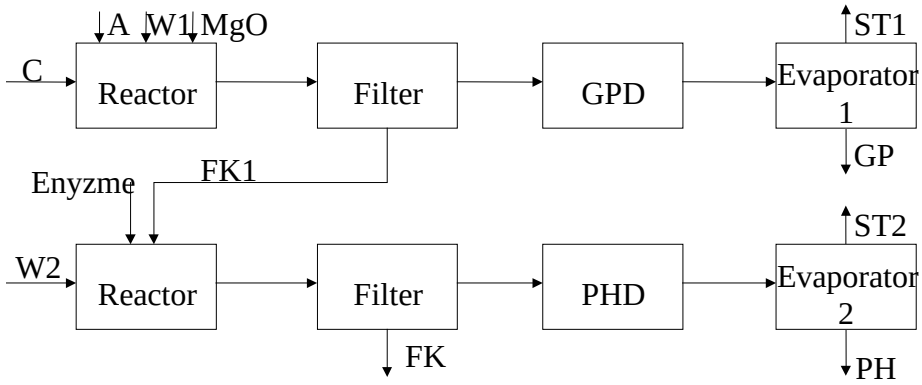
C – Chrome shavings **GP – Gelatable protein** **PH – Protein hydrolysate** **BA – n-butyl amine**	**Income from the regenerated tanning salt:** **$Na_2Cr_2O_7 . 2H_2O$ – Rs. 68/kg** $\frac{3 \times 0.0127 \times 352.04 \times 68}{151}$ = Rs.6.04/kg c ⟶ Rs.4.027/kg ⟶ Rs.2.01/kg PH

B. Detailed calculation

Details of calculations of operating cost, while processing 3 tonne of chrome shaving, are given below. Based on the results obtained in trials, the processing cost for Indian conditions was worked out. While processing 3 tonne of chrome shavings (moisture – 63.8 %), the following are estimated to be obtained: 2 tonne of gelatable protein (GP) at 30 % solid content, 1 tonne of protein hydrolyzate at 50 % solid content and 2 tonne of chrome sludge at 80 % moisture.

Mass balance calculation

For the purpose of calculation, the following scheme is used.



Where

C	Chrome shavings, 3 tonne
W1	Water, 15 tonne
W2	Water, 6 tonne
A	Amines, 0.09 tonne (3 % on the weight of wet shavings)
MgO	Magnesium oxide, 0.06 tonne (2 % on the weight of wet shavings)
GPD	Diluted gelatable protein
ST1	steam condensate from concentration of GPD
GP	Gelatable protein, 2 tonne
PHD	Diluted protein hydrolysate
ST2	steam condensate from concentration of PHD
PH	Protein hydrolyzate, 1 tonne
FK	Filter cake, 2 tonne

Total balance

$$C + A + W1 + W2 + MgO = GP + PH + FK + ST1 + ST2$$

$$3 + 15 + 6 + 0.06 + 0.09 = 2 + 1 + 2 + ST1 + ST2$$

$$19.15 = ST1 + ST$$

Dry matter balance

$$0.06 + 3x0.362 = 2x0.3 + 1x0.5 + 2x0.02$$
$$1.146 \quad / \quad 1.14$$

The difference is +0.006 tonne, which is 0.52 % error.

Material Balance in evaporator 1

Total	GPD = 2 + ST1
Dry substance	GPD x 0.05 = 2 x 0.3 $\Rightarrow$ GPD = 12 tonne

ST1 = 12 – 2 = 10 tonne

Material Balance in evaporator 2

Total	PHD = PH + ST2
Dry substance	PHD x 0.05 = PH x 0.5 $\Rightarrow$ PHD = 10 tonne

ST2 = PHD – PH = 10 – 1 = 9 tonne

Energy requirement for heating of reaction blend

$$Q_r = m.c_p.\Delta t \ ,$$

where

Q_r	heat for heating of reaction blend [J]
c_p	specific heat of reaction blend, 4.2 KJ/kg/K – estimated
Δt	temperature difference between initial and reaction temperature = 40 K
m	mass of reaction blend, 18.15 tonne

$$Q_r = 18.15x10^3 x40x4.2 = 3.0492x10^6 \text{ kJ}$$

Estimation of the heat loss in the reactor

The loss of heat (Q_l) is done:

(1) $Q_l = \alpha.S.\Delta t$, where:

α	heat transfer coefficient = 30 W/m^2/K – estimated
S	external surface of a reactor [m^2]
Δt	temperature difference between external surface of a reactor and ambient (K).

(2) $$S = \pi.d.h + \frac{\pi.d^2}{4}$$

(3) $V = \frac{\pi.d^2}{4} \Rightarrow \quad \pi.d^2.h = 4\,V\,, \qquad \pi.d.h = \frac{4V}{d}$

(4) $S = \left(\frac{4}{d} + \frac{1}{h}\right),$ h = 3d, d = 2 m (estimated)

V volume of a reaction mixture [m^3]
h height of a reaction mixture [m]
d reactor diameter [m]

(5) $S = \frac{4.33}{2} V = \frac{4.33}{2}$ x18.15 = 39.29 m^2

and hence

Heat loss Q_l = 30x30x36.81 = 35.361 kW

Heat loss in a heat insulated reactor

(6) $\alpha = \frac{\lambda}{\delta}$ where

λ - thermal conductivity of insulation – 0.01 W/m/K - estimated
δ - thickness of an insulation ÷ 1 dm.

$\alpha = \frac{0.01}{0.1} = 0.1\,W/m^2/K$

Heat loss in an insulated reactor Q_i = 30x39.29x0.1 = 117.87 W

Calculations of processing costs

Processing cost to produce 1 kg of GP, 1 kg of PH from chrome shavings and the cost for processing 1 kg of chrome shavings have been calculated below:

N_1 Cost to produce 1 kg gelatable protein
N_2 Cost to produce 1 kg protein hydrolyzate
N_3 Processing cost for 1 kg of chrome shavings

Magnesium oxide

Rate of MgO per kg: Rs. 8

$$N_1 = \frac{0.02\text{x}8\text{x}3}{2} = Rs.0.24/kg$$
$$N_2 = 0 \text{ (No MgO used)}$$
$$N_3 = \frac{0.02\text{x}8\text{x}3}{3} = Rs.0.16/kg$$

n-butylamine (BA)

Rate of n-butyl amine per kg: Rs.211

$$N_1 = \frac{0.03\text{x}211\text{x}3}{2} = Rs.9.5/kg$$
$$N_2 = 0 \text{ (No amine used)}$$
$$N_3 = \frac{0.03\text{x}211\text{x}3}{3} = Rs.6.33/kg$$

Enzyme

Cost of enzyme per kg: Rs. 2,000

$$N_1 = 0 \text{ (No enzyme used)}$$
$$N_2 = 2000\text{x}0.0003\text{x}3 = Rs.1.8/kg$$
$$N_3 = \frac{2000\text{x}0.0003\text{x}3}{3} = Rs.0.6/kg$$

Initial heating

Cost of heating Rs. 200/GJ

$$N_1 = \frac{3.0492\text{x}10^{6}\,\text{x}200\text{x}10^{-9}}{2} = Rs.0.30/kg$$
$$N_2 = \frac{0.30\text{x}9\text{x}2}{18.15} = Rs.0.30/kg$$
$$N_3 = \frac{0.30\text{x}2}{3} + \frac{0.30}{3} = Rs.0.30/kg$$

Water

Rate per kg: Rs. 0.044 per kg

$$N_1 = \frac{(15-10\text{x}0.6)(\text{Recovered water 60 \% recycle})}{2}\text{x}0.044 = Rs.0.28/kg$$
$$N_2 = (6-9\text{x}0.6)\text{x}0.044 = Rs.0.03/kg$$
$$N_3 = \frac{0.4+0.3}{3} = Rs.0.14/kg$$

Electricity

Rate of electricity per kWh: Rs. 4

Electric power input	7 kW	
Stirring time	6 hours	(GP)
Stirring time	3 hours	(PH)

$$N_1 = \frac{7x4x6}{2x10^3} = Rs.0.08 / kg$$
$$N_2 = \frac{7x4x3}{1000} = 0.08\ Rs / kg$$
$$N_3 = \frac{9x4x7}{3000} = Rs.0.08 / kg$$

Heat loss – non insulated reactor

1 kWh = 3,600 x 10^3 Joule

$$N_1 = \frac{33129x200x10^{-9}x6x3600}{2000} = Rs.0.08 / kg$$
$$N_2 = \frac{33129x200x10^{-9}x3x3600}{1000} = Rs.0.08 / kg$$
$$N_3 = \frac{33129x200x10^{-9}x9x3600}{3} = Rs.0.08 / kg$$

Evaporation

$$N_1 = \frac{10x2.25x10^6 x200x10^{-9}}{2} = Rs.2.25 / kg$$
$$Rs.0.98 / kg\ *$$
$$N_2 = 9x2.25x10^6 x200x10^{-9} = Rs.4.05 / kg$$
$$Rs.1.76 / kg\ *$$
$$N_3 = \frac{2.25x2 + 4.05}{3} = Rs.2.85 / kg$$
$$Rs.1.24 / kg\ *$$

*three steps evaporator.

Annex-4

INTERACTIVE MEETING WITH DR. KOLOMAZNIK, UNIDO CONSULTANT ON ENZYMATIC DIGESTION OF CHROME SHAVINGS

MINUTES OF THE MEETING

8 AUGUST 2000	**CONFERENCE HALL**
1430 hours	**TNPCB Building, Chennai-32**

A meeting was held in the Conference Hall of TNPCB Building to facilitate useful interaction between representatives of by-product industry, scientists & researchers and Dr. K. Kolomaznik, UNIDO consultant. A list of participants is enclosed:

Mr. A. Sahasranaman gave a brief account of the problems faced by the tanning industry in the disposal of tanned and untanned solid wastes and the various options available for the utilisation of these wastes. Underlining the quantitative limitations in the use of wet blue shavings in leather board manufacture, he observed that the other option for the utilisation of the waste as practised in some parts of the country, particularly, in and around Calcutta is the preparation of "fertiliser". However, the technology adopted is too crude and environmentally unacceptable. He introduced Dr. Kolomaznik to the participants and informed them of the work done by him in Czech Republic and the USA in the conversion of wet blue shavings into useful by-products by enzymatic digestion.

SSK, on behalf of the Consultant, made a presentation of the following pilot trials carried out by the consultant in CLRI and IIT.

1. Preparation of gelatable protein (GP)
2. Preparationof protein hydrolysate (PH)
3. Preparation of NPK fertiliser
4. Utilisation of the chrome-containing filter cake as reducing agent in the preparation of basic chromium sulphate from dichromate.

The following points were highlighted during the presentation:

- Different types of wet blue shavings were used in the trials. Shavings yielded by goat skins and cow hides were studied closely. It was found that goat shavings whose particle size is small were found easy to digest. The time taken for digestion in reactor was less in the case of goat shavings.
- All the three processes, namely, preparation of GP, PH and NPK fertiliser do not leave behind any solid or liquor wastes. The filter cake containing chrome and organic contaminants can be used as a reducing agent in the preparation of BCS from dichromate.

- The filter cake which contains MgO can also be used to precipitate spent chrome liquor in the chrome recovery process.
- A wet blue sheep skins tanned with BCS prepared from dichromate using filter cake as reducing agent was shown to the participants. The shrinkage temperature of the tanned skin was determined as 118^{o}C.
- Samples of GP, PH (in solution), filter cake and GP (spray drying) were placed before the participants.

Copies of transparencies used by SSK during the presentation are enclosed.

The participants were interested to see the samples and note details of process.

Mr. Gnanavadivel of Naina Glue, Sriperumbudur showed interest in the preparation of gelatable protein (GP) and took samples of GP and protein hydrolysate for analysis in his laboratory.

Dr. Prakash Rao of Prakash Feed Mills, Kancheepuram and his technical consultant Dr. Muralidhara Rao met Dr. K. Kolomaznik in RePO prior to the interactive session and expressed inability to try preparation of protein hydrolysate or NPK fertiliser from wet blue shavings as the method and process were not commercially feasible in Indian conditions.

Mr. Krishnaswamy, Consultant, Anand Chromates stated that use of chrome shavings as reducing agent in the preparation of Basic Chromium Sulphate had been tried in the past in many countries including India and the results were inconsistent but added that digested shavings could perform consistantly. He offered to use the chrome-containing filter cake as reducing agent in Anand Chromates if the filter cake was available in bulk quantities.

The scientists of CLRI were interested to know details of laboratory analysis of the by products. The reports on lab analysis, as received from SGS general laboratory, were shown to them.

INTERACTIVE MEETING WITH DR. KOLOMAZNIK, UNIDO CONSULTANT ON ENZYMATIC DIGESTION OF CHROME SHAVINGS

Venue: Conference Hall, TNPCB Building Date: 08 August 2000

Time: 1415 hours

#	**Name**
I. Manufacturer of animal protein	
1.	Dr. DVR Prakash Rao, Director, Prakash Feed Mills P. Ltd.
2.	Dr. Muralidhara Rao, Consultant, Prakash Feed Mills P. Ltd.
II. BY-PRODUCTS MANUFACTURER	
3.	Mr. D. Gnanavadivel, Naina Glues
4.	Mr. KG Krishnaswamy, Anand Chromates
5.	Mr. P. Subba Raj, Vpn Gelatin Factory
6.	Dr. V. Mohan Kumar, Vpn Gelatin Factory
7.	T. Arumugam, Asia Glues and Chemicals Pvt. Ltd.
III. Leather Board manufacturers	
8.	Mr. C.M. Zafarullah, Secretary
9.	Mr. Mohd. Riaz
IV. CLRI	
10.	Dr. P.G. Rao, Dy. Director, CLRI
11.	Mr. Srinivasan, Scientist, CLRI
12.	Dr. N.K. Chandrababu, Scientist, CLRI
13.	Mr. R.A. Ramanujam, Scientist, CLRI
14.	MR. R. SUTHANTHIRARAJAN, SCIENTIST, CLRI
15.	MR. BV RAMABRAHMAN, SCIENTIST, CLRI
V. ILIFO	
16.	Mr. Burkhard Peil
VI. RePO UNIDO	
17.	Mr. A. Sahasranaman
18.	Mr. Solomon Sampathkumar

1. PREPARATION OF GELATABLE PROTEIN

Input (% based on weight of shavings)	**Equipment required**	**Reaction parameters**	**Output**
Chrome shavings (50% moisture) 500% water 2% Magnesium oxide 3% Isopropyl-amine (or) n-butyl amine	Reactor with stirrer and heating arrangement Filter (vacuum filter is preferable; bag filter will do)	Temperature 65-70^{o}C pH 9.0 Duration 5 hours.	Gelatable protein

Total mass balance:

Chrome Shavings 30 kg + Water 150 kg + IPA 1.2 kg + MgO 0.6 kg ⟶ GP (5% solid) 108 kg + Filter cake (85% moisture) 56 kg

181.8 kg ⟶ 164 kg (Loss due to evaporation 17.8 kg – 10%)

2. PREPARATION OF PROTEIN HYDROLYSATE

Input (% based on weight of chrome shavings)	Equipment required	Reaction parameter	Output
Filter cake Water Isopropylamine (if necessary to adjust pH 9.0) Enzyme (0.05% on weight of shavings)	Reactor with stirrer and heating arrangement Filter (vacuum filter is preferable; bag filter will do)	Temperature 70^{o}C pH 9.0 Duration 2 to 2 ½ hours	Protein hydrolysate Filter cake

Total mass balance:

Filter cake 50 kg + Water 65 kg + Enzyme 0.015 kg ⟶ Protein hydrolysate (5.7% solid) 81 kg + Filter cake (88% moisture) 31 kg

3. PREPARATION OF ORGANIC FERTILISER

Input (% based on weight of chrome shavings)	Equipment required	Output
Chrome shavings **500% Water** 3.6% Potassium hydroxide KOH 1.7% Magnesium oxide MgO 2.3% Phosphoric acid H_3PO_4 0.05% Enzyme	Reactor with stirrer and heating arrangement Filter (vacuum filter is preferable; bag filter will do)	Organic fertiliser Filter cake

Details of reactor:

Chrome shavings + Water + Potassium Hydroxide + **Magnesium Oxide** → Run in reactor to reach a pH 12.0
Duration 2-3 hours
Temperature 70^{o}C

Add Phosphoric acid → To reduce pH to 9.0

Add Enzyme → Temperature 70^{o}C
pH 9.0
Duration 1 hour

Add Phosphoric acid → **To adjust pH to 7.0**

Filter the reacted mixture

3. PREPARATION OF ORGANIC FERTILISER (Contd.)

Input (% based on weight of chrome shavings)	**Equipment required**	**Reaction parameter**	**Output**
Filter cake Water Isopropyl amine (if necessary to adjust pH 9.0) Enzyme (0.05% on weight of shavings)	Reactor with stirrer and heating arrangement Filter (vacuum filter is preferable; bag filter will do)	pH 9.0 Temperature 70^{o}C Duration 2 to 2 ½ hours	Organic fertiliser Filter cake
Phosphoric acid		pH 7.0	

Total mass balance:

Filter cake 40 kg	+	Water 60 kg	→	Organic fertiliser (3.25% solid) 58 kg	+	Filter cake (83% moisture) 26 kg
		100 kg	→	84 kg		**Loss due to evaporation 16 kg**

4. SUMMARY OF PROCESSING COSTS

Items	Production cost Rs./kg		**Cost of processing of chrome shavings** Rs/kg	**Unit cost (Rs./kg)**	**% C**	Remarks
	GP	pH				
Magnesium oxide	0.24	0	0.16	8	2	-
n-butyl amine	9.5	0	6.33	211	3	
Water	0.2	0.03	0.14	0.044	500[1] 200[2]	[1]GP [2]PH
Enzyme	0	1.8	0.6	2,000	0.03	
Initial heating	0.30	0.30	0.30	Rs.200/GJ[3]	-	[3] estimated, Rs.150 /GJ in CR
Stirring	0.08	0.08	0.08	Rs.4/kWh	-	-
Heat loss	0.08	0.08	0.08	Rs.200/GJ	-	Non insulated reactor
Heat loss	0.0002	0.0002	0.0002	Rs.200/GJ	-	Insulated reactor
Evaporating[4]	2.25	4.05	2.85	Rs.200/GJ	-	[4] one step evaporator
Evaporating[5]	0.98	1.76	1.24	Rs.200/GJ	-	[5] three steps evaporator
Total	12.65	6.34	10.55	-	-	One step evaporator
	11.38	4.05	8.93 [a]	-	-	[a] three steps evaporator
	11.31	-	8.86 [b]	-	-	[b] insulated reactor
Replacement of n-butyl amine by MgO	3.51	-	4.45	-	6	One step evaporator
	2.24	-	2.84 [c]	-	6	[c]Three steps evaporator

C – Chrome shavings
GP – Gelatable protein
PH – Protein hydrolysate
BA – n-butyl amine

Income from the regenerated tanning salt:
$Na_2Cr_2O_7 . 2H_2O$ – Rs. 68/kg

$$\frac{3 \times 0.0127 \times 352.04 \times 68}{151} = \text{Rs.6.04/kg c}$$

⟶ Rs.4.027/kg ⟶ Rs.2.01/kg PH

Annex- 5 Relevant scientific data

1. Density of hot air

This can be estimated from the general ideal gas equation:

$$\rho = \frac{P.M}{R.T}$$

where

P pressure of hot air in the dry sprayer, 10^5 Pa
M molecular weight of air, 28.8 D
T average temperature of inlet air in the dry sprayer, 423 K
R universal gas constant = 8,314 J/kmol/K

Substituting introduced values we obtain:

$$\rho = \frac{10^5 \text{x} 28.8}{8314 \text{x} 423} = 0.81\, kg/m^3$$

2. Estimation of heat transfer coefficient

heat transfer coefficient of a thin film evaporator is calculated as follows:

$$\text{Heat transfer coefficient } \alpha = \left(\frac{4}{3}\right)^{\frac{4}{3}} \left(\frac{\rho^2 \lambda^3 \pi dg}{4 m_s \mu}\right)^{1/3}$$

Where,

ρ density of a dilute protein hydrolyzate (1,000 kg/m^3, estimated)
λ thermal conductivity of a dilute protein hydrolyzate, 0.65 W/m/k
d inner diameter of a tube where a filmed evaporation takes place (0.1 m)
m_s mass flow of steam (condensate) from evaporator ($4.3/10^3$ kg/s – experimental determined)
μ dynamic viscosity of dilute protein hydrolyzate (2cP = 2.10^{-3}Pas).

Putting numerical values in above question we receive:

$$\alpha = \left(\frac{4}{3}\right)^{\frac{4}{3}} \left(\frac{10^6 \text{x} 6.51^3 \text{x} 10^{-3} \pi .10^{-1} \text{x} 9.81}{4 \text{x} 10 \text{x} 2 \text{x} 10^3 \text{x} 4.3 \text{x} 10^{-3}}\right)^{1/3} = 1.38 kW/m/K$$

3. **Specific capacity of hot air: 1.84 kJ/kg/K**

4. **Universal gas constant, R: 8,314 J/kmol/K**

5. **Molecular weight**

Item	Molecular weight
Cr_2O_3	151.99
C_3H_5NO	71.079
H_2SO_4	98.077
$Na_2Cr_2O_7$. 5 H_2O	352.043
MgO	40.311
Na_2O	61.979
H_2O	18.015
Na_2SO_4	142.041
$MgSO_4$	120.374
$Cr_2(SO_4)_3$	392.177
Sucrose, $C_{12}H_{22}O_{11}$	343.5053