

CHAPTER – IV

➤ RESULTS AND DISCUSSION

CHAPTER-IV

IV.1 Characterization of repeated soak liquors

The detail descriptions of analysis of soak liquors obtained after every step of soaking of wet-salted skins have been done in Chapter III.4, the findings have been presented in Appendix A: in the table nos. A-1 to A-4 and the same has also been presented as bar charts in Appendix C: as Fig. Nos. A-1 to A-4. The sample no. denoted as E-01 in all tables and figures is represented the soak liquor obtained from conventional soaking operation. Whereas sample nos. denoted by ε -01 to ε -11 in all tables and figures are represented the soak liquors obtained after each repetition of soaking in the same water, i.e. ε -01 stands for soak liquor after first soak, ε -02 stands for soak liquor after second soaking of w/s skin in the same soak liquor, similarly ε -11 stands for soak liquor sample after eleventh time repetition of soaking in the same soak liquor. The results obtained from the different experiments are being discussed separately below:

IV.1.1 Discussion on results of TDS in different soak liquor samples

The substances what may dissolve in the soak water, from wet-salted raw skins, are mainly the common salts used for preservation along with some soluble proteins, fats, globular proteins and any soluble matter present in the dirt and dung adhered to the skin surfaces. The soak liquors of samples E-01 and ε -01 are practically same as both obtained after first soaking, thus the values of TDS of those are found more or less same as 68.7 and 70.5 g/L respectively. After that, the TDS values of sample nos. ε -02 to ε -11 are gradually increased because more and more common salt from wet-salted skins got dissolved in the soak liquor. The soak liquor was found to be almost saturated in respect

of common salt after eleven number of soaking. At this stage, i.e. in the sample no. ε -11, the TDS value of the liquor is found 388.6 gm/L which is enormously high as compared to the conventionally obtained soak liquor (max. 50 g/L, Rajamani, S. JILTA-2001). The increment of TDS value from one sample to next sample is not uniform. As can be seen in samples ε -01 to ε -06, the increment is quite large as compared to samples ε -07 to ε -11. It is mainly due to gradual depletion of the dissolving capacity of soak water and gradual reduction of available soluble materials as the reducing raw weight of the samples are used for the experiment.

IV.I.2 Discussion on results of Salinity (as NaCl) in different soak liquor samples

The salinity of the samples is found gradually increasing from ε -01 to ε -11, more or less in the same manner as TDS. Salinity contents of sample nos. E-01 and ε -01 are found very close i.e. 65.52 and 70.2 g/L respectively due to same reason as stated in the section IV.1.1. Also the increment of salinity for sample nos. ε -01 to ε -06 are found to be higher in comparison to the same value of the samples ε -07 to ε -11 due to same reasons as stated for the explanation of TDS value in the earlier section. It has been found that 316 g pure Sodium chloride salt is required to make 1-liter saturated solution with density 1.19 g/c.c. at 20°C ⁵⁵. Where as in the sample no. ε -11, the salt content is found 366.21 g/L which is considerably high as compared to the value referred above i.e.: 316g/L. There may be two reasons for that: firstly, the temperature of soak liquor was $30 \pm 2^{\circ}\text{C}$, thus solubility of salt will be slightly higher than the value at 20°C and secondly, the experimental result obtained is an indication of all chloride salts present in the sample whereas the standard figure cited above represents only sodium chloride. Another interesting information is obtained from the comparisons of corresponding data of TDS

and Salinity of the same sample, that is around 99% TDS is contributed by salinity alone. It has been found that TDS content of soak liquor sample is significantly correlated with its salinity content having a positive correlation between them (0.98) at $p < 0.05$.

IV.1.3 Discussion on results of BOD_5^{20} in different soak liquor samples

The BOD_5^{20} value of the samples has been found increasing with the increasing of sample nos. as the gradual solution of more biodegradable matters in the soak liquor for after each repetition of soaking. It is interesting to note that the pattern of increment of BOD is not similar to the increment pattern of salinity and TDS value. The difference in in the BOD_5^{20} value between sample no. ε -01 and ε -06 is nearly 630 mg/L and the same between sample no. ε -06 and ε -11 is nearly 1340 mg/L. Thus the average increment of the biodegradable matter content from one sample to next sample in the first half zone (ε -01 to ε -06) is nearly half of the average increment of the same for the second half zone (ε -07 to ε -11). The source of biodegradable matter in the soak liquor is mainly globular proteins along with some loose fibrous proteins and some biomass contaminated organic debris on the surfaces of wet-salted skins. Since the solubility of proteins, especially globular proteins, is increased with the increase of salinity of water, more and more proteins are dissolved in the soak liquor with higher salinity. Thus the salinity of soak liquor continuously increased gradually with the repeated recycling of soak liquor. This is the main reason to have more average increment of the BOD value in the second half zone. It may be mentioned here that addition of certain salts in the right amount can selectively precipitate some proteins, while others remain in solution. This effect is particularly observed with the application of Ammonium Sulphate $[(NH_4)_2SO_4]^{73}$.

IV.1.4 Discussion on results of COD in different soak liquor samples

COD values of the samples are also increased from sample nos. ε -01 to ε -11 and following more or less same pattern of the BOD values. The COD values in the sample liquors depend on the amount of bio degradable as well as non- biodegradable organic matters present in a certain volume of liquor. The COD value of sample no. ε -01 is very much close to the same value of sample no. E-01 due to same reason as stated for TDS and Salinity. The difference between the values of COD from ε -01 to ε -06 is nearly 60,000 mg/L and the same is found nearly 85,000 mg/L from ε -06 to ε -11. In this case also the average increment of COD values follows almost the same pattern of BOD. The source of non-biodegradable matters in the soak liquors is mainly grease and dust present in the raw skins and the same contributes to COD. The experimental findings regarding the values of COD reflects the fact that accumulation of either biodegradable or non-biodegradable or both have been increased with the increasing salinity of soak liquor. The solubility of biodegradable matter have been found more in saline water, it has been already discussed in the Chapter IV.1.3. In spite of that, it has been detected four species of salt loving microorganism in final soak liquor of which one is true halophilic and three are halotolerent. The optimum growth of true halophilic bacteria has been found at nearly 300 g/L salt concentration of media which can be added as another reason for higher increment of BOD_5^{20} and COD values from the samples nos. ε -06 to ε -11. In this context, it worthwhile to mention here that the salinity of soak liquor sample no. ε -06 has been found 304.2 g/L in experimental determination.

IV.2 Evaluation of physical and chemical properties of leathers

The physical and chemical properties of the finished lining-type medium-soft leathers, obtained from both conventional and experimental methods of processing (soaking), are measured as per IS specification. The detail procedure of testing has been described in Chapter III under section III.5. Sample nos. E-01 to E-11 are the leather samples denoted the finished leathers, processed conventionally from the right sides of the wet-salted skins and the sample nos. ε -01 to ε -11 are denoted the same, processed experimentally i.e. reusing of soak liquor, from the corresponding left sides of the wet-salted skins. The results of experimental findings have been shown in Appendix B: in the table nos. B-1 to B-13 and their respective column charts are shown in the Appendix D: as figure nos. from B-1 to B-13. Table no. B-14 in Appendix B represents the average value of different physical and chemical properties of leather obtained by conventional method of soaking and proposed method of soaking. Table nos. from B-1 to B-8 are represented the physical properties of finished leathers like, thickness and length along the back bone, shrinkage temperature, water vapour permeability, tensile strength and percentage elongation at break, stitch tear strength, grain crack strength and ball bursting strength, absorption of water and dry-rub & wet-rub colour fastness respectively. Similarly, figure nos. from B-1 to B-8 are represented the bar charts of respective physical properties of finished leathers in Appendix D, whereas table nos. B-9 to B-13 represent different chemical properties of finished leathers like, volatile matter content, ash content, chloride (as NaCl) content, sulfate (as Na₂SO₄) content and chromium (as Cr) content respectively and figure nos. from B-9 to B-13 are represented corresponding

bar charts. In all tables and figures, the results of the two similar sample numbers, one is obtained from conventional way of soaking and another is obtained from repeated soaking i.e. E-01 and ε -01, E-02 and ε -02.....E-11 and ε -11 are placed adjacently for better understanding and comparison. The results obtained from different experiments are being discussed separately bellow.

IV.2.1 Discussion on results of Thickness and Length along the back bone

The variation of thickness and length along the back-bone between same nos. of samples are found 0.0 - 0.1mm and 0.00 – 90mm respectively. Thickness and length are two dependent variables of nature of the raw skins i.e. genus of the animal, the place of birth and husbandry, the age at slaughtering, anti-mortem diseases and also the nature & amount of chemical treatment during processing. As such the variations in thickness and length between two samples of same number what already stated above are found very minimum. On the other hand all the physical properties are expressed either in per unit thickness or in per unit cross-sectional area, thus this type of variation would be a factor for changing any results in very slight amount. Chemical properties of finished leathers are least dependent on thickness and length of the finished leathers.

IV.2.2 Discussion on results of Shrinkage Temperature of finished leathers

Shrinkage temperature of finished leather is the temperature at which most of the cross-linkages between two adjacent collagen fibers via chromium starts to rupture and results in shrinkage of fiber and consequently the leather. Thus, shrinkage temperature is mainly dependent on the strength and number of cross-linkages present in a unit volume of collagen network. From experimental data, it has been found that shrinkage temperatures of experimental samples (as denoted by ε) are as much as 4 -8°C greater than the same of

conventional samples (as denoted E). Generally chrome tanned leathers show the shrinkage temperature 100 or slightly more than 100°C as it has been found for samples denoted by E ($104.5 - 111^{\circ}\text{C}$). But the shrinkage temperatures of samples denoted by ε have found remarkably high i.e. $110 - 116^{\circ}\text{C}$. This enhancement of shrinkage temperature appears due to high salinity of experimental samples for repeated soaking prior to chrome tanning. The astringency of the chrome liquor decreases due to addition of salt therefore to inactivate all the active groups of collagen, more chrome complexes will be needed, thus the Cr_2O_3 fixation by the collagen will be increased⁷⁴. This higher chrome oxide fixation with the collagen is one of the important and primary criteria for increasing probability of higher cross linking. Although the salt concentration is increased with the repetition of soaking in the same liquor as well as the salt content inside the soaked skins, yet the results of shrinkage temperature of experimental samples are not increased gradually. The average effect of salt is obtained as all soaked skins of different salt contents are processed in the same bath from the unit operation liming to chrome tanning, they got chance to attain an average higher concentration of salt. Since this average salt concentration inside the experimental pelts is higher than the conventional pelts, fixation of chrome complex obtained is higher in experimental samples and consequently higher shrinkage temperatures results.

IV.2.3 Discussion on results of Water Vapour Permeability of finished leathers

Water vapour permeability is very important property for leather specially lining for shoe. In dynamic condition, sweating is occurred continuously from feet and that sweat should be escaped out in vapour phase and also absorbed through or by the shoe lining leather for giving comfort to the wearer. Water vapour permeability and water absorption,

these two properties are not present in the polymeric materials what generally used as leather substitute. The amount of water vapour passing through the unit area of leather per unit time is measured in two span of time i.e. after 1-hr and after next 2- hrs without any break of experiment. From the experimental results, it has been found that the average permeability of experimental samples (denoted by ε) is initially little bit greater than the conventional samples (denoted by E) i.e. after 1-hr, but in the long run i.e. after another 2-hr, the results become reverse. The permeability values, after 2-hrs, of sample nos. ε -01 to ε -06 have been found nearly half of the same values of corresponding conventional samples. Whereas, the differences in value of permeability from sample nos. ε -07 to ε -11 are not so dramatic as compared to the same of sample nos. E-07 to E-11. Thus, in the long run, the salinity level in finished leather up to 98×10^{-3} % (NaCl content of ε -06), permeability value reduces considerably, and after that it becomes insignificant. After 1-hr, the minimum permeability for experimental sample and conventional sample is found 377×10^{-6} and 259×10^{-6} g/min/cm² respectively. Whereas the minimum permeability has been found lower for experimental sample than the conventional one after another 2- hrs, that is 283×10^{-6} g/min/cm² for experimental and 330×10^{-6} g/min/cm² for conventional. This anomaly may be for the salinity content of experimental samples. Since the common salt is hygroscopic in nature, thus it can absorb water vapour. In case of leather, water vapour does not diffuse through the free space only but through the material also. Thus, in the long run experiments, this absorption of water vapour by common salt present inside the leather reduces the permeability but when salt becomes saturated by moisture the effect becomes faded. However, the

permeability values of experimental samples are not poor in every respect comparing with the same of conventional samples.

IV.2.4 Discussion on results of Tensile Strength and Percentage Elongation at break of finished leathers

Tensile strength of the leather is the force per unit area of cross section required to rupture the test specimen. It is a function of the number of fibers in the collagen matrix oriented in the direction of applied force. In most of the cases, the tensile strengths of the experimental samples are found slightly greater than the conventional samples. This is mainly the variation of the thickness of finished leathers. The thicknesses of the experimental samples are found lesser than the conventional samples in most of the cases due to little bit suppression of swelling in the liming operation for samples prepared by following the proposed repeated soaking method. On the other hand, any increase in cross section during tannery operation decreases the tensile strength of the finished leather what is generally observed in samples prepared by following the conventional soaking method, as because in a given cross section the number of fibers being constant with the increase of cross sectional area the tensile strength will decrease. Although the tensile strengths of samples nos. denoted as ε and conventional samples nos. denoted as E are found within the range $107.64 - 216.56 \text{ kg/cm}^2$ and $140.58 - 240.54 \text{ kg/cm}^2$ respectively, but the average value of tensile strength of samples marked as ε is found slightly greater than the samples marked as E i.e. 169.55 kg/cm^2 for experimental and 167.64 kg/cm^2 for conventional samples. Generally the percentage elongation at break is increased with the increase of tensile strength of finished leather, this has been observed in most of the cases. But, the average value of percentage elongation at break of the

samples prepared by following the proposed soaking method has been found to be 9.66% which is a little less than that of samples prepared by following the conventional method, which is 10.15%. This little deviation may be for the individual physical quality of the raw skins.

IV.2.5 Discussion on results of Double-Hole Stitch Tear Strength of finished leathers

The double-hole stitch tear strength is measured as the force per unit thickness required for tearing apart the sample of leather between two equal holes of specific diameter and separated by a specific distance. This helps in determining the strength of small seams of leather. Thus, the double-hole stitch tear strength is very important for leather as raw materials for leather goods manufacturing. The double-hole stitch tear strength of experimental samples is found slightly less than the corresponding conventional samples in most of the cases. Generally, the leather of high tensile strength shows high stitch tearing strength, but it is not so in this case. The partial removal of interfibrillary globular proteins from skins during soaking in saline water due to salting in effect, in case of experimental samples, increases the degree of freedom of fibers inside the leather along the perpendicular direction to the applied force what improve the tensile strength. On the other hand for high stitch tearing strength the fibers are required some amount of background support from the non-fibrous materials present inside the leather. Since in conventional samples, the interfibrillary materials are removed in smaller amount than experimental samples for the avoidance of saline soaking, the stitch tearing strength is found slightly greater than experimental samples. The values of stitch tearing strength are found lowest 55.085 kg/cm-thickness and highest 98.085 kg/cm-thickness for experimental samples. Whereas, it has been found the lowest value 62.53 kg/cm-

thickness and highest value 114.925 kg/cm-thickness for the conventional samples. The average values of stitch tearing strength for experimental samples and conventional samples are found 78.70 kg/cm-thickness and 85.03 kg/cm-thickness respectively. It should be mentioned here that the minimum requirement of stitch tearing strength is 50 kg/cm-thickness as per IS specification.

IV.2.6 Discussion on results of Grain-crack Strength and Ball-Bursting Strength of finished leathers

The grain-crack strength as well as the bursting strength is an index of the overall strength of the leather. The grain-crack and ball-bursting strengths are measured by the force required to create crack on the grain and to burst out the grain per unit thickness of the leather respectively. In most of the cases the grain-crack strength of the experimental samples has been found greater than the conventional samples. The grain-crack strengths of experimental samples are found within the range 30 – 80 kg/cm thickness, whereas the same values of conventional samples are found in between 15.63 – 107.93 kg/cm thickness. But the average value of grain-crack strength is found slightly greater for experimental samples than conventional samples i.e. 52.25 and 52.11 kg/cm thickness respectively. On the other hand, average value of ball bursting strength of the experimental sample is found considerably higher than the conventional sample i.e. 78.08 and 65.91 kg/cm thickness. Since different strengths of leather are equivalent to each other, the improvement of grain crack strength automatically improves the ball-bursting strength in most of the cases. The grain-crack strength and ball-bursting strengths are mainly depended on the tensile strength and percentage elongation at break (elasticity) of the leather fibers. The tensile strength of the experimental samples are found slightly

greater than the conventional samples and stretchiness i.e. percentage elongations at break are found slightly reverse what has been mentioned in the Chapter IV under section 2.4. The cumulative effects of those are reflected from the results of grain-crack strength and ball-bursting strength of finished leather. As per tensile strength of experimental sample, the grain- crack strength should be higher than conventional samples, but the low stretchiness of experimental samples than conventional one nullified the effect and results minimal differences in grain-crack strengths.

IV.2.7 Discussion on results of Water absorption on apparent volume and weight of finished leathers

The percentage of water absorption by leather mainly depends on the void space present inside the fiber net-work and nature of chemicals (hydrophilic or hydrophobic) treated during processing of leather. For the user's comfort leather should have sufficient capacity to absorb water for absorbing sweat liberated from user's skin of contact. The percentage water absorption on both apparent volume and apparent weight of leather has been found slightly greater in experimental samples than conventional one. The results for percentage water absorption on apparent volume of experimental samples are found within the range 78.13 -104.17% after 30 minutes and 86.81 – 117.65% after 60 minutes whereas the same for conventional samples are found within 73.53 – 100% after 30 minutes and 79.66 – 112.85% after 60 minutes. On the other hand the percentage water absorption on apparent weight of the leather for experimental samples are found within the range 121.62 – 185.71% after 30 minutes and 135.14 – 228.57% after 60 minutes whereas the same for conventional samples are found within 102.56 – 164.95% and 115.38 – 175.26% after 30 and 60 minutes respectively. The average values of percentage

water absorption on apparent volume for experimental samples are found 93.54% and 104.29% and for conventional samples 85.60% and 96.06% after 30 and 60 minutes respectively. Also the average values of percentage water absorption on apparent weight for experimental samples are found slightly higher than the conventional samples i.e. 161.36% and 180.12% for experimental and 127.50% and 142.99% for conventional samples after 30 and 60 minutes respectively. All these results are focused that the void space available in the experimental samples are greater than the void space available in the conventional samples. The fact is supported by the average values of apparent densities of both experimental and conventional samples i.e. 0.58 and 0.67 g/cc respectively. Lower the apparent density of finished leather is the conformation of higher percentage of void space inside the leather. According to the apparent densities, the percentage of void space will be around 60% for experimental samples and around 50% for conventional samples⁷⁵. The extra void space in experimental samples in respect of conventional one has been formed for the removal of extra interfibrillary materials due to saline soaking. It has been mentioned in the Chapter IV under section 1.3 that soaking in saline water dissolved extra interfibrillary materials like globular proteins. On the other hand, the presence of higher amount of strong electrolyte (NaCl) in experimental samples has increased hydrophilicity of Cr-collagen matrix favouring higher water absorption than their counterpart. These are the main reasons for experimental samples to have high percentage of water absorption and low apparent density in respect of conventional samples.

IV.2.8 Discussion on results of Dry-rub and Wet-rub colour fastness of finished leathers

The test is carried out on dyed leather surface to ensure the absence of unfixed dye as well as the resistance of fixed dye against dry and wet rubbing by means of a white cloth wrapping on a pad. Dyed leather should have high degree of colour fastness. From experimental results, it has been found that both dry rub and wet rub colour fastness of experimental samples are better than conventional samples. Although the grey scale reading for dry and wet rub fastness of leathers for both experimental samples and conventional samples are found within the range 4 to 5 and 3 to 4 respectively, the average reading for experimental samples are found slightly greater than conventional one. The average grey scale readings for dry rub fastness of experimental and conventional samples are found 4.90 and 4.09 respectively and the same for wet rub fastness obtained 3.90 and 3.64 respectively. From the experimental results, it is clear that dye molecules have been fixed more rigidly with the experimental samples than conventional samples. Not only that, it is also clearly understandable by naked eye that the depth of dye is more in experimental samples than conventional one. This is ensured the greater amount of dye fixation in unit area. The salinity content of experimental samples was greater than conventional one prior to dyeing due to recycle of soak liquor up to eleven times for experimental samples. This high salinity was the main cause for high uptake and fastness of anionic dye stuff. Due to high salinity, chrome uptake and fixation were increased in experimental samples what was reflected from the results of shrinkage temperature. High chrome uptake by the pelt is also a secondary cause of greater uptake and fastness of anionic dyes in experimental samples. It will be conducive

to mention the statement of Stubbings and Strauss that addition of neutral salts does not influence the affinity of anionic dyes until these salts are present in concentrations far higher than those normally employed in leather dyeing practice. Many anionic dyestuffs penetrate chrome tanned leather completely when they are applied from a high (5%) concentrated solution of common salt⁷⁶.

IV.2.9 Discussion on results of Volatile Matter Content in finished leathers

The test is carried out to determine the percentage of volatile matter present in finished leather. The procedure has been described in the Chapter III under section 5.10. Water in the form of moisture is the main volatile matter present inside the leather along with other volatile substances what can be vaporized to escape from the leather within the temperature $102 \pm 2^{\circ}\text{C}$. In most of the cases the percentages volatile matter content of experimental samples are found less than the conventional samples. The volatile matter content in experimental samples is found within the range 13.05% - 17.40% and for the conventional samples it has been found 14.32% - 16.18%. But the average value of volatile matter content of experimental samples is found slightly less than the conventional samples i.e. 14.80% and 15.26% respectively. This slightly higher value of volatile matter content in conventional samples in respect to experimental samples may be for the higher interfibrillary matter content in conventional samples. On the other hand the interfibrillary matter present in the experimental samples is slightly less than conventional samples due to saline soaking what dissolves some extra interfibrillary materials from raw skin. The interfibrillary matter content in finished leather is one of the major factors for moisture content as well as volatile matter content otherwise the moisture content of wet-salted skin where interfibrillary materials present fully, cannot be

reduced from 30-35% to around 15% what is the moisture content of finished leather, after processing.

IV.2.10 Discussion on results of Ash Content in finished leathers

Ash content of finished leather is the measurement of inorganic materials present inside the finished leather after processing. After heating of ground-leather at $800 \pm 25^{\circ}\text{C}$ for four hour, only inorganic materials will be able to present as ash and all organic materials will be disintegrated and evaporated out far before reaching the temperature mentioned above. The detail procedure of determination has been described in the Chapter-III under section 5.11. As per experimental results, percentage ash content of all experimental sample nos. has been found greater than the corresponding conventional samples nos. The ash content of experimental and conventional samples is found within the range 8.48 – 13.21% and 8.35 – 10.04% respectively. The average values of percentage ash content of finished leather of experimental and conventional samples are found 11.41% and 9.05% respectively. Due to saline soaking of experimental samples, the accumulation of common salt inside the leather has been increased gradually with the number of samples. This is the one factor for the high ash content of experimental finished leathers. On the other hand, shrinkage temperature of experimental samples have been found higher than that of corresponding conventional samples which ensure the more amount of chromium fixation with the experimental samples. This should be another reason for finding high ash content in experimental finished leathers.

IV.2.11 Discussion on results of Chloride (as NaCl) Content in finished leathers

As per experimental results, the chloride content of experimental samples have been found gradually increasing pattern with the increasing sample nos. On the other hand, all

conventional samples are found with more or less same chloride content. It should be mentioned here that the percentage value of chloride content in finished leather has been found in the range $10^{-3}\%$ figure which is very small. Thus, this tiny content of salt could not create any adverse gross physical and chemical changes among the experimental samples rather some better effect on Cr (III) and dye uptake. The percentages of chloride content in experimental and conventional samples are found within the range 81 – 163 and 60 – 75 multiplied by $\times 10^{-3}\%$ (w/w) respectively. The average value of percentage chloride content for experimental samples is found $107.36 \times 10^{-3}\%$ (w/w) and the same found for conventional samples found to be $65.64 \times 10^{-3}\%$ (w/w). The high chloride content of experimental samples in respect of conventional samples has found due to repeated use of soak liquor in soaking operation for experimental samples. The wet-salted goat skins of experimental samples have been soaked in the liquor of gradually increased salinity with the increased sample nos. and accumulated more and more common salt in the finished leathers. Since all wet-salted goat skins of conventional samples are soaked at a time in fresh water, the percentages of chloride content of conventional samples have been found more or less equal.

IV.2.12 Discussion on results of Sulphate (as Na_2SO_4) Content in finished leathers.

The sulphate salts have been used in the process in two unit operations i.e. Deliming and Tanning. Ammonium sulphate has been used in the deliming operation and basic chrome Sulphate has been used in the tanning operation. Besides these point sources there is always a considerable amount of sodium sulphate in the basic chrome sulphate powder as a byproduct. According to the recipe for both experimental and conventional samples, the amount of ammonium sulphate and chromium sulphate has been offered same in those

unit operations. Yet the percentage of sulphate-salt content in experimental samples has been found slightly greater than conventional samples from the experimental data. Individually all experimental sample nos. are found slightly greater sulphate content than the corresponding conventional sample nos. The percentage of sulphate-salt content for both experimental and conventional samples are found within the range 2.71 – 4.01% with average value 3.52% and 2.62 – 3.23% with average value 2.94% respectively. The presence of extra sulphate salts must be for the higher consumption of basic-chrome-sulphate and also may be for higher consumption of ammonium sulphate in experimental samples than conventional samples. The reason for higher consumption of chromium due to salinity has already been explained in the Chapter IV under section 2.2. The extra sulphate ions from extra basic-chrome-sulphate consumed by the experimental samples in respect of conventional samples have raised mainly the sulphate-salt content.

IV.2.13 Discussion on results of Chromium (as Cr) Content in finished leathers

As per experimental results, all the experimental sample nos. is found with slightly higher chromium content than the corresponding conventional sample nos. The percentage of chromium content in both experimental samples and conventional samples are found within the range 3.52 – 3.74% and 3.32 – 3.61% respectively. The average value of percentage chromium content in experimental samples is found slightly greater than the average value of the same in conventional samples i.e. 3.63% and 3.44% respectively. This extra chromium content in experimental samples have been found mainly for the high salinity of the pelt due to recycling of soak liquor in the soaking operation. For this extra chromium content in experimental samples, the shrinkage temperatures have been found slightly greater than the conventional samples. The reason behind the high

consumption of chromium in pelt due to salinity has already been explained in the Chapter IV under section 2.2. On the other hand it should be mentioned here that the difference in average value of sulphate content between experimental and conventional samples is found 0.58% which is little bit more in comparison with the difference of average value of chromium content i.e. 0.19% in between experimental samples and conventional samples. Because 0.19% rise of chromium is equivalent to 0.52% rise of sulfate (as Na_2SO_4) considering the empirical formula of BCS as $\text{Cr}(\text{OH})\text{SO}_4$. From this result, it is clear that the experimental samples are being accumulated some extra sulphate salts from other sources except chrome tanning. The other sources should be ammonium sulphate in deliming operation; perhaps the consumption of ammonium sulphate has been increased due to extra salinity of experimental samples than conventional one and may be the presence of Glauber's salt as a reaction product of BCS.

IV.3 Discussion on desalination of final soak liquors

The spent liquor of soaking after 11th repetition looks muddy and contains some un-dissolved solids, suspended solids and dissolved solids (mainly common salt). This liquor has been treated for recovery of salt. To separate out the course materials present in the liquor, the liquor is filtered through a porcelain funnel fitted with perforated bed of pore diameter 200 – 300 μm . Then the liquor was treated with alum [$\text{Al}_2(\text{SO}_4)_3$, 18 H_2O] for separation of suspended and coagulating substances , by filtration. The filtered solution contains mainly common salt of concentration around 290 g/L and some organic substances of main component are dissolved protein. Common salt can now be recovered by evaporation. The detailed procedure of treatment has been described in the Chapter III under section III.6.

IV.3.1 Discussion on results of Alum treatment of final soak liquor

The filtered solution after alum treatment is very transparent in nature having turbidity 0 NTU (previously standardize the instrument at 0 against turbidity of distilled water), which indicates the absence of any suspended material. It has been found that 180-200ml Alum [Al₂(SO₄)₃, 18 H₂O] solution of 5000 ppm strength is very much effective for 1000ml soak liquor at 25 ± 2°C to have a clear solution of 0 NTU. The total time of the process like stirring, settlement and filtration has been found around 4 hr. The loss of volume of soak liquor by means of Alum dosing and consequent filtration has been found around 6%, which very natural. It has been found that the curd like muddy filtrate from 1000 mL soak liquor can be dried completely within 5-6 days at 25 ± 2°C and 60-70% R.H., some suitable use of this material can be thought of. The weight of filtrate has been found 70 – 80 g from per 1000 mL soak liquor.

IV.3.2 Discussion on results of solar evaporation of filtered soak liquor

Solar evaporation has been followed for desalination. As because the other processes of desalination are not suitable for saturated salt solution, the reasons behind these have been discussed in Chapter-II under section II.10.2. Method of solar evaporation is considered most appropriate for recovery of salt from the filtered soak liquor. From the results of experiment; it has been found that 290-300 g salt can be recovered from 1000 mL final soak liquor by solar evaporation. It has been found that for effective solar evaporation the solution should be spread over an area having depth not more than 2-3 mm. Under exposure of sunlight with atmospheric temperature around 25°C and relative humidity around 60%, it has been found that the total time of evaporation required 12 hr. approximately. The process can be improved by using the method suggested in

Chapter III under section III.6.3. The whiteness and crystal size of the common salt can be improved by treating with Calcium Oxy-Chloro Chloride ($\text{Ca}(\text{OCl})\text{Cl}$), or bleaching powder and controlling the rate of evaporation respectively. The salt obtained from solar evaporation may be reused for preservation of raw hides and skins or in pickling operation, further study in this regard is worth pursuing. Another improved method of solar desalination of saturated brine what is undergoing for study has been discussed in chapter III under section III.6.3.

In the method of studied, soak liquor is not allowed to mix with the composite waste water, as a result the volume of effluent and also the pollution load will be reduced considerably. The proposed method of soaking can be treated as a unique one to be followed for pollution reduction, as chloride content (as Cl^-), of the effluent will be as compared to the effluent from the tannery where conventional method of soaking is followed. Further the Total Dissolved Solids (TDS) and Total Solids (TS) content of the effluent will also be reduced. Not only that, this method can reduce the final effluent quantity by 20 – 30 percent volume which means the load on Common Effluent Treatment Plant (CETP) for treatment of tannery waste water will be reduced considerably. The tannery effluent is considered problematic for treatment due to its high salinity, hence a reduction of salinity by about 50 – 60% following the proposed method should be considered as a boon. As is observed from the study the final effluent from the tannery operation will improve both quantitatively and qualitatively.