A MATHEMATICAL MODEL FOR UNSTEADY STATE SALT DIFFUSION FROM BRINE-CURED CATTLEHIDES*

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Abstract

Removal of salt from brine-cured cattlehides occurs during soaking operations in the tannery beamhouse. A mathematical model has been developed to predict the rate of diffusion of salt from a hide as a function of time and soaking conditions. The model can be utilized in the design or evaluation of unsteady state (nonequilibrium) batch soaking operations. The model results from the solution of the differential equation for one-dimensional unsteady state diffusion. Results are presented showing the comparison of model predictions of soaking batch salt concentration or hide salt content with the following data: (a) laboratory bench scale studies under controlled conditions, (b) pilot plant beamhouse treatment of cattlehides in drums, and (c) the rapid soaking operation in the ERRC continuous beamhouse processing line.

Introduction

Soaking is a basic unit operation in the preparation of hides for tanning and processing conditions have been developed over years of practical experience. As the goal of soaking is to restore the hide as closely as possible to its natural state just after slaughter, the salt deposited during the curing process must be removed. Although phenomena such as rehydration and removal of denatured globular proteins are important to the quality of the finished leather and affect the choice of soaking conditions, salt removal can be considered the primary requirement in the selection of process parameters.

A comprehensive study of soaking has been reported by McLaughlin (1). Variables investigated included soaking time, composition of soak water, temperature, nature of proteins removed, and bacteriological aspects. The primary emphasis of this and other studies was the effect of equilibrium composition of the soak solution on the aforementioned variables. Little information is available in the literature on the rate of diffusion of salt from brine-cured hides under nonequilibrium conditions.

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In engineering terminology, soaking as it has been historically practiced is a batch equilibrium process and as such can be characterized by two major variables, soaking time and float ratio (1b soak solution/lb raw hide, usually expressed as a percentage). A recent limited survey of tannery soaking conditions* revealed a wide variation in both soaking times and float ratios. Soaking times ranged from 4 to 12 hr with float ratios of from 100 percent to 250 percent. Multistage soaking, in which hides were refloated in fresh solutions, was also practiced.

In contrast, hide soaking in the continuous beamhouse process (2, 3) under development in the Engineering Science Laboratory of the Eastern Regional Research Center (ERRC) is a continuous steady state operation with nonequilibrium salt diffusion from the brine-cured cattlehides. Steady state conditions in the hide soaking vats are maintained by countercurrent water flow. For design of such a system for a specific degree of hide salt removal, knowledge of the rate of salt diffusion from the hide as a function of time and soaking conditions is essential.

This paper will describe the development of a mathematical model for the prediction of salt removal from brine-cured cattlehides as a function of time and process variables. The model arises from the analytical solution of the diffusion equation applied to hide soaking. It has application to soaking operations designed on the basis of salt removal with the realization that other factors may influence the final choice of soaking conditions. The model was verified by comparison to controlled laboratory studies and tested against experimental pilot plant data on cattlehides. The model can be useful in the design of continuous steady state soaking conditions, the comparison of alternative batch soaking schemes, or as a tool in the optimization of soaking operations on the basis of soaking time or water usage.

Model Development

Theoretical description of hide salt diffusion. The model was developed for fleshed, brined, and salted cattlehides. The surface salt content is variable, usually in the range of 10-30 percent in excess of the brined salt content. The distinction between the surface salt and internal (brine deposited) salt is important since hide salt diffusion is viewed as the superposition of two separate processes: 1) the rapid diffusion of crystalline salt from the hide surface (surface salt diffusion) and 2) the slow diffusion of the internal salt to the surface and then into the surrounding solution, referred to as the bulk solution. Surface salt diffusion is treated as if the surface salt was a thin slab of salt in contact with the bulk solution and salt removal occurs via molecular diffusion of sodium chloride. Its mathematical description is essentially the same as that of internal salt diffusion and will not be described in detail here.

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Internal salt diffusion is considered to be diffusion through a porous medium with a variable and unknown pathlength. The approach taken was to solve the diffusion equation representing one-dimensional unsteady state diffusion with the appropriate hide geometry and utilizing an "effective diffusivity" to account for the restricted mobility and variable pathlength of salt molecules in the hide. A schematic diagram representing the geometry of the diffusion process is presented in Figure 1. Physically, the hide is visualized as a one-dimensional slab

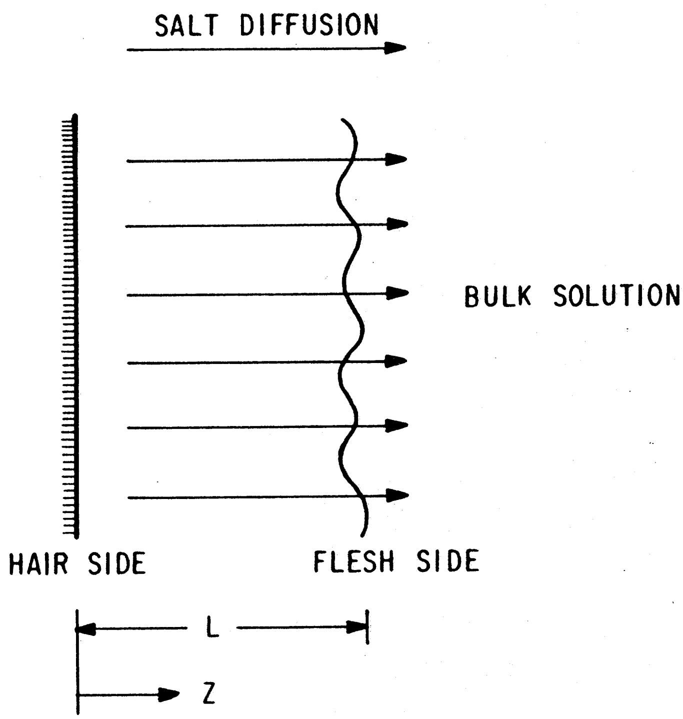

FIGURE 1. — Schematic representation of salt diffusion in cattlehides.

of thickness 1 through which salt diffuses to the bulk solution. It is assumed that salt diffuses out the flesh side only since the epidermis acts as a barrier to soluble substances (1). This fact was confirmed by laboratory experiments in which each surface of the hide was alternately coated with an insoluble gel material. Other assumptions were: a) diffusion from the edges of the hide was neglected. b) Diffusion only occurs in the z direction. c) The bulk solution is well mixed. d) The water in the hide is initially saturated with salt. The diffusion equation for unsteady state diffusion in one direction is:

$$\frac{\partial C_A}{\partial t} = D_A' \frac{\partial^2 C_A}{\partial z^2} \qquad (1)$$

with boundary conditions:

$$C_A = C_A^* \text{ at } z = 1$$
$$C_A = C_{A_S} \text{ at } z = 0$$

and initial condition:

$$C_A = C_{A_S} \text{ at } t = 0$$

where

C_A= concentration of salt in the water in the hide at any z and time
C_{A_S}= salt saturation concentration
C_A^*=bulk solution salt concentration
D_A'= effective diffusivity of salt in the hide

Details of the solution will not be discussed. The procedure for the solution involved Laplace transformation and series expansion and was generally similar to that reported elsewhere (4). In dimensionless variables the solution is:

$$C = \sum_{n=0}^{\infty} \left[\operatorname{erfc}\left(\frac{1-Z+2n}{2\sqrt{T}}\right) - \operatorname{erfc}\left(\frac{1+Z+2n}{2\sqrt{T}}\right) \right] \qquad (2)$$

where erfc is the complementary error function and

$$T = \frac{D_A' t}{1^2} \qquad \text{Fourier Number}$$

$$Z = z/1 \qquad \text{Dimensionless Distance}$$

$$C = \frac{C_{A_S} - C_A}{C_{A_S} - C_A^*} \qquad \text{Dimensionless Concentration}$$

The flux of salt at the surface of the hide, N_{A_S}, is defined as the amount of salt leaving the hide per unit area and time and is expressed as:

$$N_{a_s} = D_A' \left. \frac{\partial C_A}{\partial z} \right|_{z=1} \qquad (3)$$

Evaluation of the derivative yields the average surface flux over the interval t = 0 to t = t.

$$\overline{N_{a_s}} = 2\sqrt{\frac{D_A'}{\pi t}}\ (C_{A_S} - C_A^*) \qquad (4)$$

For time intervals in which C_{A_s} and C_A^* do not appreciably change, eq. (4) can be used to calculate salt removal from the hide as a function of time by multiplying the flux by the area of hide undergoing soaking and the elapsed time.

Modelling approach. Equation 4 is the basis of the model. The model can be used in many ways, depending upon the soaking operation to be modelled and the desired results. For example, the salt concentration in the float can be predicted as a function of time or, through a mass balance, the hide salt concentration can be calculated. The prediction requires treating salt flux as a constant for short time intervals and summing the incremental fluxes iteratively until a desired time or bulk salt concentration was reached. Parameters needed for the model are the total surface area of hide undergoing soaking, the initial hide salt and moisture contents (if prediction of hide salt content is desired), the volume of float, and the effective diffusivity, D_A'. In experiments in which the soaking of hide pieces or single sides was modelled, the hide surface area was measured directly; otherwise, an assumed value of 25 ft^2/side was used. The value of D_A' used was 3.75 x 10^{-5} cm^2/min and was calculated from laboratory data according to procedures given by Crank (5). C_{A_s} was calculated by assuming the initial uptake of soak solution completely mixed with the salt and water in the raw brine-cured hide. Computer algorithms were constructed to perform the iterative computations.

Experimental

Bench scale model verification studies were conducted in 3-liter beakers in which measured and weighed hide pieces were submerged in well stirred soaking solutions. Periodically, samples of the soaking solution were analyzed for chloride to follow the rate of diffusion of salt from the hide. Salt concentrations were calculated from Baumé specific gravity measurements or from chloride concentrations which were determined by the Mohr method (6).

Moisture and chloride contents of hide were determined on the same sample. Hide sampling areas were selected near the neck of the hide along either the back or belly. Diced hide samples were vacuum dried at 70°C for 16 to 18 hr and the weight loss calculated as moisture content. The diced samples were then ground in a Wiley* mill to pass a 10-mesh screen, weighed into porcelain dishes, and ash-

*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

ed at 550°C. The chloride content of the hydrolyzed ash was also determined by the Mohr method. In solutions containing sulfide, hydrogen peroxide was added to oxidize the sulfide before chloride determinations. All analyses were performed in duplicate.

Results

The usefulness of any mathematical model of a particular process is a direct function of the range of conditions under which it acceptably predicts process performance. Model verification studies were conducted on experimental data over a wide range of soaking conditions. Comparison of model prediction to experimental data will be presented for three types of data: (1) bench scale experiments of short duration, (2) pilot plant data from the continuous beamhouse processing time, and (3) pilot plant data from full beamhouse treatment (through reliming) of hides. In addition, results of two simulation studies will indicate potential uses of the model in the design or optimization of soaking operations.

Model verification. As knowledge of salt diffusion rates from hides in the early stages of soaking is important in the design of countercurrent steady state soaking operations, bench scale tests of up to several hours in duration were conducted under a variety of conditions. Figure 2 summarizes some of these results in-

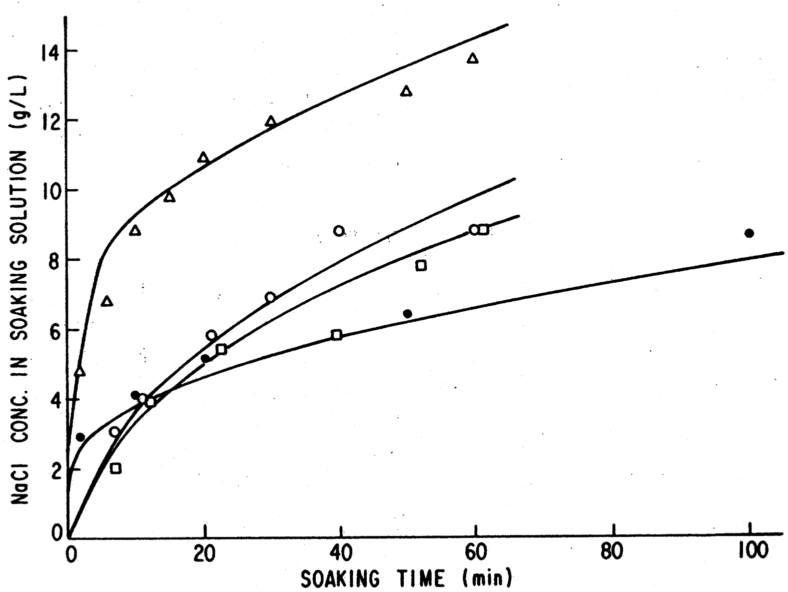

FIGURE 2.— Bench scale model verification studies. Solid lines are model predictions. Points are experimental data: ●, 234 g hide in 2.775 1 water; □, 340 g hide, surface salt removed, in 2.5 1 water; O, 306 g hide, surface salt removed, in 2.5 1 water, Δ, 344 g of same hide as in □, surface salt removed, then 14.5 g NaCl worked into hair side, in 2.5 1 water.

cluding experiments designed to determine the effects of surface crystalline salt. For soaking times of approximately 1 hr or less, the surface salt must be considered since it accounts for a significant portion of the total salt removed from the hide. Considering the rapid changes in bulk solution salt concentration in these experiments, agreement between the model predictions and experimental data is reasonably good.

Data is being collected at ERRC regarding the changes in hide salt content as a function of time and processing conditions. Hide salt content is a convenient way to evaluate a soaking operation or to compare different soaking conditions. Salt content data from five experimental runs of the continuous beamhouse processing line are presented along with model predictions in Figure 3. For these short duration soaking experiments, there is some variation in the experimental data but, again, agreement is satisfactory.

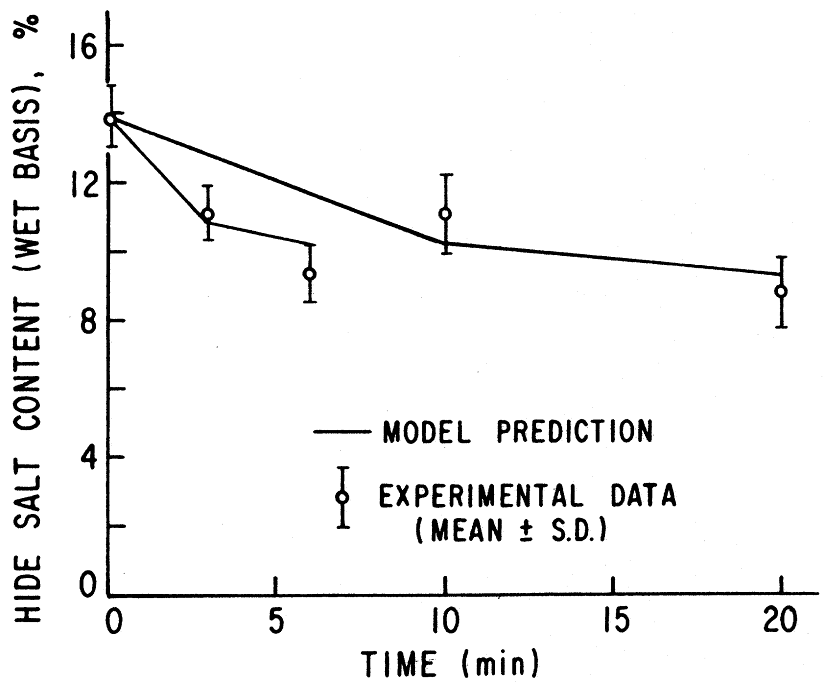

FIGURE 3.— Model prediction of continuous beamhouse process soaking data (5 experimental runs). Soaking operations conducted in two 1000-gal baths of 10 percent NaCl and 4 percent NaCl, respectively.

Although originally developed to predict the salt flux from hides under none-quilibrium conditions, the model can be applied to equilibrium or near equilibrium operations. Figures 4 and 5 represent a test of the model on ex-

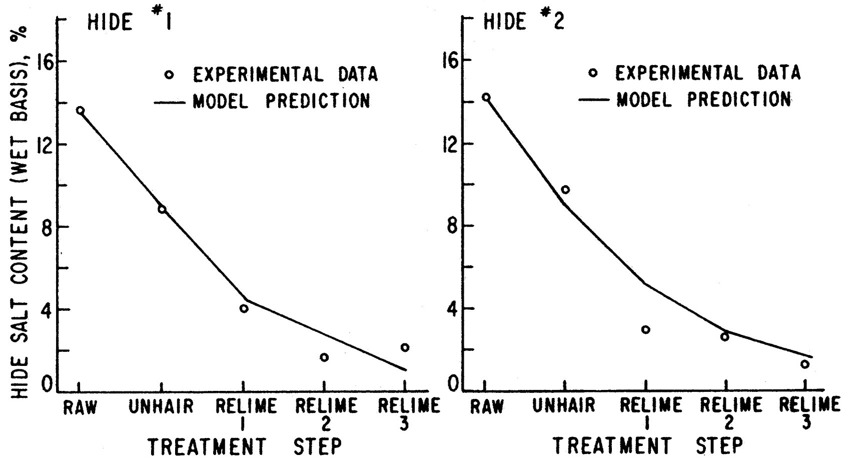

FIGURE 4. — Salt removal in beamhouse processes — model prediction vs. experimental data. Process conditions: Unhair, 10 min in 1000-gal tank of 10 percent NaCl, 10 min in 1000-gal tank of 4 percent NaCl, 10 min in 1000-gal tank of 1.6 percent Na_2S; reunhair, 2 hr, 100 percent float, 2.3 percent lime, 1 percent Na_2S, 85°F; relime, two 2-hr soaks in 100 percent float, 1 percent lime, 85°F, followed by 16 hr relime, 100 percent float, 2-1/2 percent lime, 85°F. (Float and chemical percentages based on raw hide weight.)

perimental data for full sides which were processed in the continuous beamhouse line and then carried through reliming in a hide processor (total capacity, 600 lb) or drum/in pilot plant facilities at ERRC. Multistep operations with nonuniform float ratios and soaking times are easily analyzed by model algorithms. In general, the model predictions are good; for example, predicted vs. actual residual hide salt contents after 20 hr of soaking (hides initially at 14 percent salt) were .76 vs. .56 percent, 1.10 vs. 2.0 percent, and 1.95 vs. 1.22 percent for the three hides examined in two separate experiments. A major source of error in these experiments can be attributed to the model assumption that salt diffusion only occurs through the flesh side. When the epidermal layer of the hair side of the hide is removed during reunhairing or reliming, additional surface area becomes available for salt diffusion. Thus, the model would tend to predict a higher salt content after unhairing.

In a similar experiment, hide salt content data was obtained from an actual tannery process conducted in the pilot plant facilities of ERRC. This process was also modelled and comparison to actual data is shown in Figure 6. The excellent agreement indicated in these results is an example of the applicability of the model to batch equilibrium soaking processes. In summary, verification studies under a variety of soaking conditions have provided confidence that the model can predict with a reasonable degree of accuracy the degree of hide salt removal in beamhouse soaking operations.

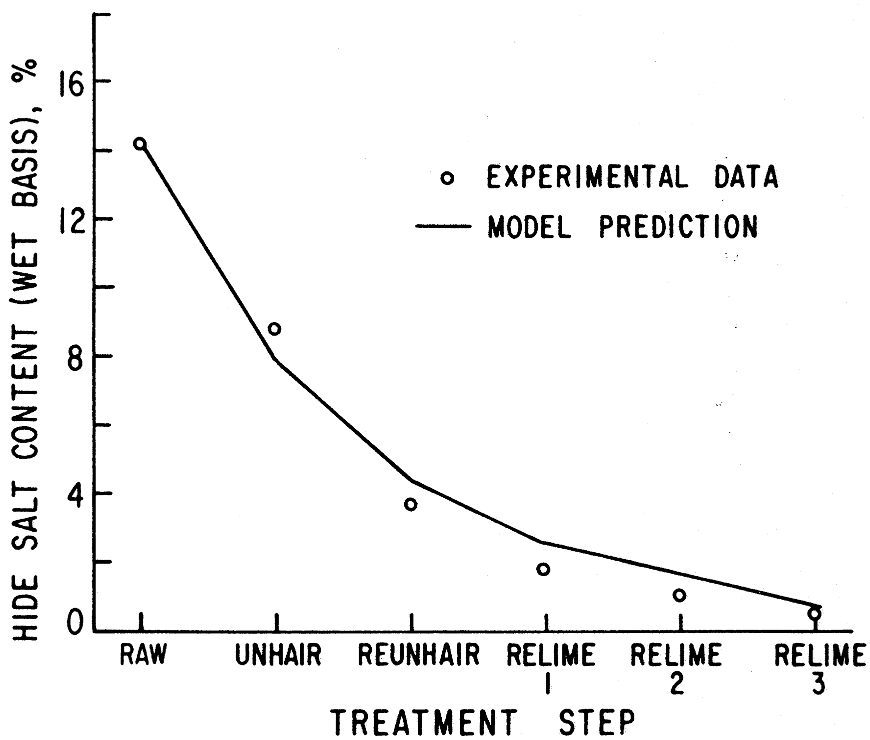

FIGURE 5. — Salt removal in beamhouse processes — model prediction vs. experimental data. Process conditions: Unhair, 10 min in 1000-gal tank of 10 percent NaCl, 10 min in 1000-gal tank of 4 percent NaCl, 10 min in 1000-gal tank of 6.1% Na_2S; reunhair and relime same as in Figure 4.

Applications of model. As previously described the model calculates salt flux from brined cattlehides as a function of time and with appropriate computer algorithms the model can be used for many applications. Two examples will be presented: the design of a two-stage countercurrent steady state hide soaking operation and the analysis of operational variables in batch soaking processes.

The continuous beamhouse process is based upon nonequilibrium hide soaking of 20 min in a two-stage countercurrent system operated at steady state. The process is shown schematically in Figure 7 which also gives the tank sizes and operating capacity of the pilot plant facility at ERRC. It was necessary to determine the soaking bath salt compositions and countercurrent water flow rate for steady state operation of the system at any desired hide salt removal rate. It can be shown that for any specific salt composition of the hide leaving the second soaking bath, there exists one unique set of soaking bath salt compositions and countercurrent water flow rate. Referring to Figure 7 in which the problem is formulated, the solution procedure can be summarized as follows: for any desired

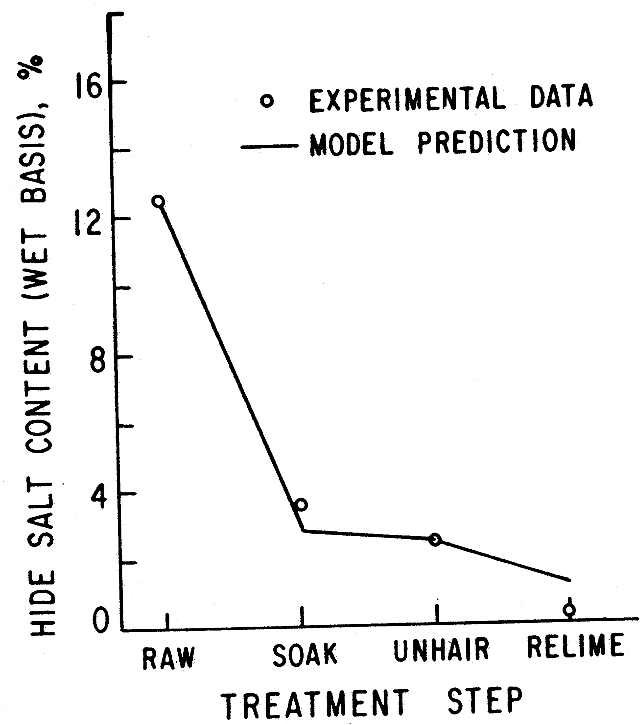

FIGURE 6. — Comparison of model prediction vs. experimental data for a commercial soaking process. Processing conditions were: soak for 12 hr at 200 percent float and 68°F, unhairing for 13 hr at 26 percent float and 90°F, relime for 7 hr at 150 percent float and 85°F.

hide salt composition leaving soak 2, W_{total} can be calculated using an assumed average initial hide salt composition. Then, in a trial and error procedure, C_1 is selected and W_1, W_2, (the salt removal rates in soak 1 and soak 2, respectively), and C_2 are calculated from the model and the equations presented in Figure 7. If the calculated values of W_1 and W_2 do not sum to W_{total}, a new value of C_1 is selected and the procedure repeated until such agreement is reached. Results for several desired hide salt compositions are presented in Table I. Based on other requirements of the continuous beamhouse process, hide salt removal to a level of 8-9 percent (wet basis) was desired. Hence, soak 1 and soak 2 concentrations of 100 g and 40 g NaCl/1 were chosen.

For a practical application of the model to existing tannery processes the effect of time, float ratio, and number of soaking stages (i.e., refloats) was examined in a computer simulation study. The "base case" for comparison is the result of the soaking operation represented in Figure 6; soaking at 200 percent float for 12 hr of hides initially 12.6 percent NaCl (wet). Utilizing the same hide data, model

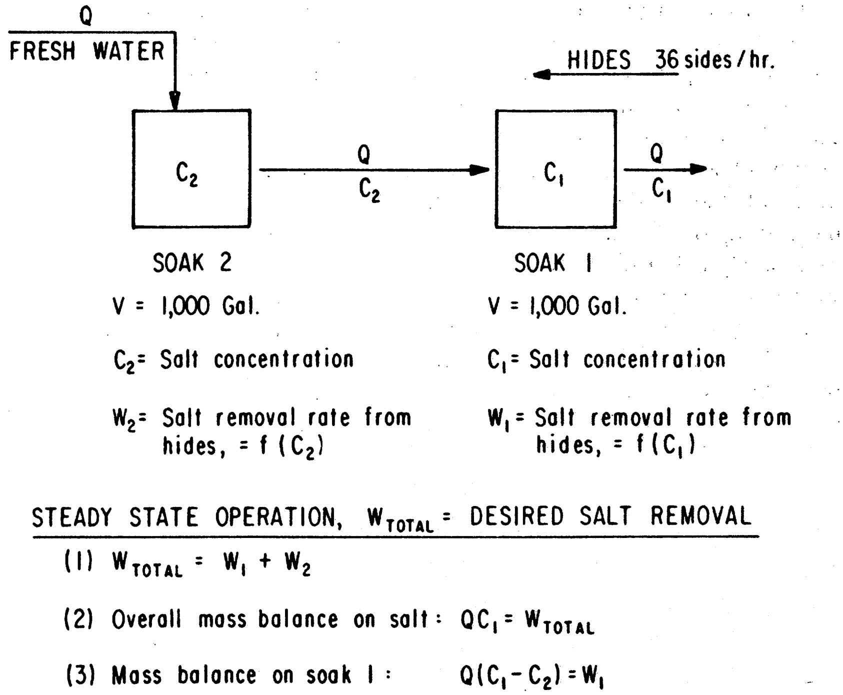

FIGURE 7. — Schematic representation of soaking in continuous beamhouse process operated under continuous steady state conditions.

TABLE I

DESIGN OF A TWO-STAGE COUNTERCURRENT STEADY STATE SOAKING OPERATION[a]

Desired salt content of hide after soaking (percent, wet basis)	Soaking Bath Design Parameters[b]		
	C_1(g NaCl/1)	C_2(g NaCl/1)	Q(gal/hr)
8.0	35	12	130
8.45	100	40	40
9.0	173	82	19
10.0	281	175	7

[a]Tank size = 1000 gal; 36 sides/hr.
[b]C_1= salt content of 1st soaking bath.
C_2 = salt content of 2nd soaking bath.
Q= countercurrent water flow rate.

predictions for varying float ratios, times, and number of stages were generated. The effect of these variables is shown in Figure 8 in which the base case and two other possible processes are compared on the basis of percent of initial salt removed from the hide. In one such comparison, the soaking time for equivalent salt removal was reduced from 12 hr to approximately 7 hr by utilizing the same amount of water in a two-stage operation rather than a single float. Based on these and other model simulation studies, the following general statements can be made: if rapid removal of salt is desired, the use of two to three stages each of approximately 2-3 hr duration is optimal, while if minimization of water usage is a constraint, only marginal improvement in salt removal is gained beyond a total water usage of 2 lb H_2O/lb hide whether staging is utilized or not. Staging is most beneficial after 2-3 hr soaking, since the rate of diffusion falls off rapidly after that time. This study has demonstrated how a knowledge of the rate of nonequilibrium salt diffusion can be applied to the selection of batch soaking conditions with either time or water usage as constraints.

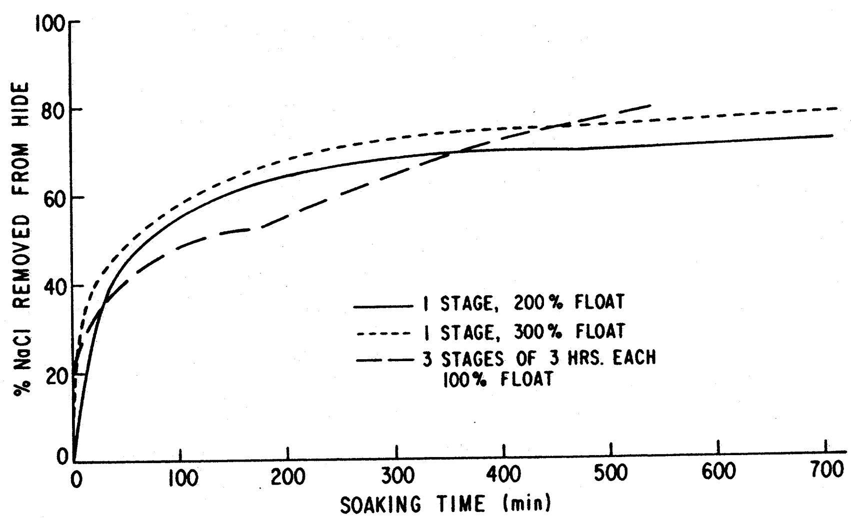

FIGURE 8. — Model simulation study of soaking variables.

Discussion

The mathematical model for salt diffusion from brined cattlehides presented herein was developed from the basic equation describing unsteady state diffusion and was shown to be applicable to a wide variety of soaking operations. As many factors affect the properties of hides relative to their behavior in soaking, the general agreement between the *shape* of the predicted curves and experimental data is strong evidence that the basis of the mathematical model is sound. Mathematical description of nonequilibrium diffusion phenomena in heterogeneous foodstuff materials has only recently been attempted (7, 8). The value of D_A' is the most important determinant of model accuracy. The brine-cured cattlehides utilized in this study were from several sources, were of variable quality, and underwent long periods of storage. The variation of D_A' with hide thickness was investigated but no general improvement in model accuracy was obtained by correction of D_A' for differing hide thicknesses. The D_A' used in this study was based upon a hide thickness of .5 cm. Larger values of D_A' (representative of thicker hides) would result in model predictions of lower hide salt content or conversely, higher salt concentrations in soak waters. No attempt was made to investigate the effect of other hide variables such as initial moisture content on the value of D_A' although such variables may have an effect on the effective diffusivity.

It is important to recognize the limitations of the mathematical model. It has been developed for soaking operations involving brine-cured hides prior to depilation although it can be applied to long term beamhouse processing operations (through reliming) with reasonable accuracy. This model implicitly assumes soaking to be a salt removal operation; other factors such as globular protein removal and other conditioning requirements were not considered. The ultimate uses of such a model lie in the design and control of countercurrent nonequilibrium soaking operations in tannery beamhouses or the analysis of multiple batch soaking processes.

Acknowledgments

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