# Mathematic Description of Biological Changes in the Cured Hides Soaking

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*Abstract:* - The advantages and possible complications of mathematical simulations – indirect modelling of tanning processes are discussed in the introduction. As an example of deterministic models of mathematical simulation, a diffusion model for the cured hide soaking operation is presented. The minima of the main operation costs are determined, following from their dependence on the consumption of the soaking liquid – technological water. The minimum of the costs depends, besides economical and technological parameters, on the values of physical constants – the speed constant of the dissolving of the surface solid salt (pre-soak washing), the transport parameter that enables a qualified approximation of the duration of the soaking operation itself, and the effective diffusion coefficient of salt in the inner volume of the cured hide. A possible occurrence of concentration shock is modelled, as well as a method of its prevention. Experimental methods for the determination of physical constants are also presented.

*Key-Words:* - Cured hide, Soaking, Concentration shock, Diffusion

## 1 Introduction

Increasing prices of energy, chemicals and water, as well as serious problems relating to environmental protection[1], and especially sustainable leather manufacturing as a topic of growing importance, require rationalization and optimization measures within the leather industry[2,3]. As early as 1972, Corning[4] published an extensive article summarising his own long-standing experience of chemical engineering work in the tanning industry. Corning[4] dealt with the potential application of theoretical tools of chemical engineering for rationalising the tanning processes. He came to the conclusion that mathematical simulation of chemical processes, as the chief tool of chemical engineering, was not used in tanning practice at all. This fact was very sharply criticised and proposals were put forward for which stages of tanning production mathematical simulation can be fundamentally put to effect.

Progress can be actively aided in this manner, particularly in introducing automation, continuation and robotisation of tanning operations. It is a fact that apart from exceptions[5,6,7], theoretical tools of chemical engineering have not found application in tanning industry rationalisation. We have dealt with the given problems for almost twenty years and present here the results in connection with soaking cured hide.

Optimization, rationalization and innovation are connected with the simulation of tanning processes. Since in many processes during which raw hide is transformed into leather the exact mechanism is not generally known, it is necessary to carry out experimental measurements under laboratory conditions. For the above mentioned tasks, it is necessary to elaborate such models that would reflect the real manufacturing process. There are two possible ways of projecting these models: direct and indirect modelling.

Using direct modelling, we choose such an experimental procedure in the laboratory, which (without calculating and mathematical analyses of physical or physical-chemical processes) gives us a direct answer as to how the manufacturing process will behave. Using indirect modelling, we focus on obtaining such mathematical models, which allow the description of the behaviour of a technological process, possibly of an apparatus, on the basis of the characteristics of elementary processes (transfer phenomena, physical-chemical processes, the kinetics of chemical reactions, etc.). The procedure proceeds from the data that is independent of the used experimental apparatus and its regime. In this case, the laboratory apparatus can significantly differ from the real machine as can the conditions of laboratory measurements.

Despite the above mentioned disadvantages, during the last few years a method has been elaborated which allows, in many cases, suggesting an optimization of the processing process with the use of highly abstracted data, i.e. indirect modelling. The main advantage of indirect modelling is the fact that to obtain the data it is possible to use an apparatus, which of course must allow exact measuring, but no demands are made on the apparatus' relation to the properties of the operation device. It is possible to propose a general procedure from the measured data and it is not necessary to subordinate the methodology to the research on the type of the operation device, which does not prove to be the best choice until the research has already started. Using direct modelling it is often necessary to proceed by stages.

It is necessary to change the methodology of the experiment according to how the idea about the mechanism of the operation is being specified the most. Therefore, we use the indirect modelling methodology everywhere where it can be used, because it is progressive in its economic efficiency, speed and it often allows carrying out optimization interventions in cases where the direct modelling is unsuccessful due to the problem complexity and the large amount of experimental work.

It can be stated that during a practical proposal of optimization and innovation of wet processes it is necessary to select sensibly the research method. The co-operation between a tanner technologist and a processing engineer plays an essential role here. The effort to use indirect modelling at all costs may take the attention away from the principal aim and may prolong the way to achieving the aim. On the other hand, the direct modelling method is sometimes experimentally more demanding; it requires the construction of a larger amount of apparatus and, which is the most important, it requires carrying out most of the research in trial equipment. At the same time, it is necessary to become aware that in most cases, the direct modelling method is never able to fulfil the conditions of a complete identity of operation in the industrial practice and in a laboratory; therefore, the method is only a certain approximation.

It is always necessary to know what conditions the industrial practice and laboratory differ in, which can be very often determined correctly with the use of a model based on mathematical processing of a problem given. With practical proposing of devices for wet processes (and not only for them) it will be probably useful to combine suitably both methods and to determine the optimal combination from a detailed analysis of a specific operation both from engineering and processing technology points of view. This task requires an optimal co-operation of representatives of two seemingly different professions: process engineering and tanning technology.

In our contribution we will deal with indirect modelling of cured hide soaking, because to the proposal of every controlling system precedes a detailed analysis of the technological process. The analysis consists of finding out the static and dynamic properties of the process, which can be carried out with the use of one of the methods of experimental identification and subsequently the mathematical modelling. Within this analysis, a qualitative and quantitative description of a given process is carried out, which includes both its structure and the parameter values. Via this description, an evaluation of the existing way of control can be made, particularly an examination of the suitability of the used control system in relation to the given technology. The description also helps to create controlling algorithms of the individual parts of the control system, as well as to propose the information flows and to determine modification proposals for the technology and controlling procedures of the conception of a complete solution. The implementation of the analysis is usually very difficult and complicated. In many cases, it is necessary to simulate the given system by computer in order to reveal the real or principal source of trouble in control[8]. For the tanning industry, it is characteristic that in many cases the processing used to be carried out without a previous elaborate analysis of the technological process.

The aim of the technological process analysis is to determine the basis for the determination of (if possible) optimal properties of the controlling system, as well as to propose a procedure alternative and to determine preliminarily the technical-economic significance. Hottinger[9] states that an automation of the various process vessels to achieve consistent quality is recognised as essential for modern tannery. Sorting, measuring, quality check and stacking – all in line to avoid extra use of labour and chemicals is a point to focus on.

Soaking of cured hide – two effects have to be achieved with cured hide – cleaning up of the hide and rehydration of the interior of the hide that is connected with the removal of salt as a preservative chemical. Salted hides require several washes with fresh water under strong mechanical agitation for proper cleaning. A drum can be used and the wash float should be changed at least twice with fresh water after 30 to 60 minutes of drumming. Air-dried hides and pelts have to be carefully soaked in long floats, at first very carefully without movement. After rehydrating enough to become flexible they can be drummed. The starting point for drumming is a matter of experience[10].

Salt is removed with water usually in three steps: first, a pre-soak, followed by a period of soaking and finally, a post-soak wash. We use electron microscopy so that soaking parameters of de-salting volume and time are optimised. If we do not do that, the fine structure can be damaged. We have also made estimates for the overall cost of the operation based on electricity power consumption by the agitator motor and the volume of soak water.

## 2 Theory

Main operating costs $N$ are given by the sum of costs of electric power $N_E$ for rotation by electric motor and the cost of consumed technological water ($N_W$ - desalination solution). The cost of electric power is proportionate to the unit price of electric energy $(K_E)$ in USD/kWh, input power $(P)$ in kW, and operating time $(\tau)$ in hours. The cost of soaking water is the product of the unit price of water in USD per cubic meter and the volume $(V_0)$ of water in cubic meters.

$$N = N_E + N_W = P\, K_E\, \tau + V_0\, K_v \tag{1}$$

This function is a proper cost function for optimizing and control process that results in the optimum operating conditions.

### 2.1 Soaking

After the removal of the surface salt raw hide contains a virtually saturated solution of sodium chloride which has to be removed. The mathematical model of soaking is the diffusion model[5,11]:

$$\frac{\partial c}{\partial \tau}(x,\tau) = D\frac{\partial^2 c}{\partial x^2}(x,\tau), ...0 < x < b \tag{8}$$

$$\tau > 0$$

$$c(x,0) = c_p \tag{8a}$$

$$\frac{\partial c}{\partial x}(0,\tau) = 0 \tag{8b}$$

$$-DS\frac{\partial c}{\partial x}(b,\tau) = V_0\frac{\partial c_0}{\partial \tau}(\tau) \tag{8c}$$

$$c(b,\tau) = \varepsilon c_0(\tau) \tag{8d}$$

$$c_0(0) = 0 \tag{8e}$$

$$y = \frac{V_0 c_0}{V c_p} = Na\frac{c_0}{c_p} \tag{8f}$$

The control algorithm of soaking depends on the initial value of the diffusion coefficient related to the content of dry mater in raw hide. The criterion deciding whether soaking in a question will be long term, medium term or short is the numerical value of the transport parameter $\Lambda$, defined as a ratio of the effective diffusion coefficient D to pore half length $(a)$ squared, according to which sodium chloride proceeds.

$$\lambda = \frac{D}{a^2} \tag{9}$$

$$\frac{c_0(\tau)}{c(\infty)} = \frac{2}{\sqrt{\pi}}\frac{1+Na}{Na}\sqrt{\lambda\tau} \tag{10}$$

$$c(\infty) = \frac{c_p}{Na+\varepsilon} \tag{11}$$

When controlling soaking in practice, a suitable sampling period is selected of the dependence of dimensionless concentration on the square root of time, transport coefficient $\lambda$ is calculated employing equation (10)[12]

Following values of $\lambda$ determine:

$\lambda \le 2\times10^{-5}s^{-1}$ – long – term soaking
$2 < \lambda \le 10\times10^{-5}s^{-1}$ – medium – term soaking
$\lambda > 10\times10^{-5}s^{-1}$ – short – term soaking

In practical soaking control, the procedure is essentially the same as in the control of washing before soaking but different in finding $\lambda$, or value of diffusion coefficient, as the only identifying parameter of soaking by means of equation (10). In some cases, particularly when moisture content in the hide and salt is great, there can be a danger of damage to subsurface fibrous structure owing to concentration shock. In the case hide contains a saturated solution of salt and is immersed in pure soaking liquid, rapid desalination of surface layers takes place, salt concentration drops to zero in a very short time and salting occurs in the following as a consequence of diffusion flow see fig. 2, curve 2.

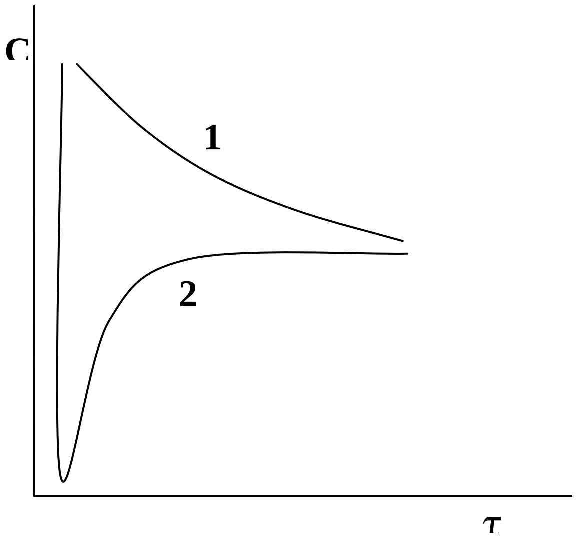

Fig. 1 Rapid (2) and slow (1) desalination

In order to avoid that, the almost saturated solution of salt presented on the drum is not to be removed after the pre soak wash. But through flow washing with a very small stream of pure water the high concentration gradient of salt in the inner hide volume is very small near the surface see fig.2, curve 1.
These sudden changes (curve 2) can inflict damage upon fibrous structure see fig. 3.

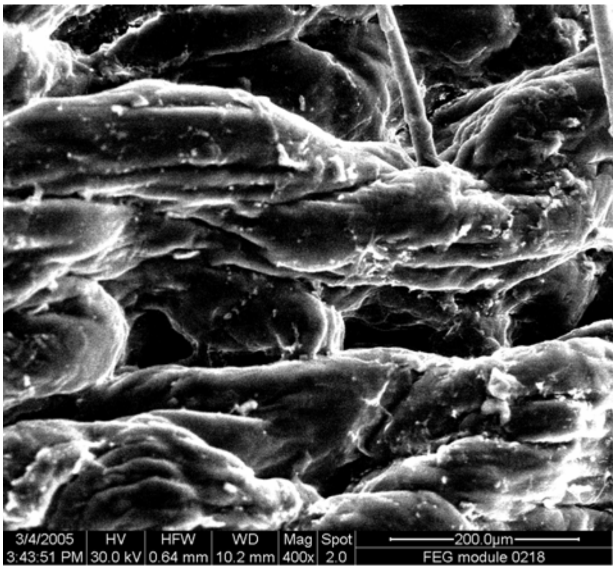

Fig. 2 Border parts of raw hide - extensive damage

Quantitative description changes only the initial and boundary conditions in our diffusion model, i.e.+ $\dot{V}c_0(\tau)$, is added to the right side of relationship (8c) and, initial condition (8d) will not equal zero but $c_0(0)=c_{0p}$. The fine hide structure that is closed to a surface is saved. See fig. 4.

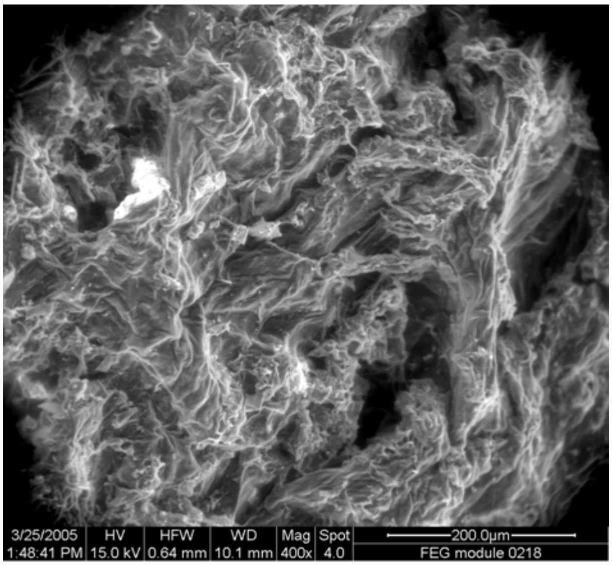

Fig. 3. Border parts of raw hide - without damage

## 2.2 Post-soak wash

Washing after soaking can be also described by the diffusion model as with main soaking see equations (8 – 8f). Dividing equation (1) by volume of cured hide *(V)*, we obtain:

$$\frac{N}{V} = n = \frac{K_E P\tau}{V} + K_V Na \qquad (10)$$

The greater the dimensionless consumption of water *(Na)*, the smaller the washing time required for given degree *y* (effectiveness of washing process). This fact results in the dependency of specific costs *(n)* on total water consumption $V_0$ or on its dimensionless expression *Na* exhibiting a minimum. Our task is to find this minimum and hence also find the optimum time of the washing operation, which corresponds to the lowest main operating costs, and in this sense to control the process. Time *(τ)* in equation (10) depends on dimensionless water consumption *(Na)* and this implicit dependency is determined for the desired washing degree *(y)* by equations (8 – 8f). In order to determine the dependency of main specific operating costs on total water consumption $V_0$, and thereby also determining their minimum and optimum time, we elaborated a computer program enabling us to determine the mentioned dependency [13]. The program contains input data as follows:

***Technological parameters*:**

| | |
|---|---|
| Load of cured hide (washed material) | $V$ [m$^3$] |
| Half-thickness of cured hide washed pieces | $b$ [m] |
| Input power of washing drum electric motor | $P$ [kW] |
| Required degree of washing process | $y$ [1] |

***Economic parameters:***

| | |
|---|---|
| Unit price of water | $K_V$ [USD m$^{-3}$] |
| Unit price of power | $K_E$ [USD (kWh)$^{-1}$] |

***Physical parameters:***

| | |
|---|---|
| Porosity of solid (washed) phase | $\varepsilon$ [1] |
| Value of effective diffusion coefficient of washed-out component | $D$ [m$^2$ s$^{-1}$] |

The following Fig. 5 (Cost function) indicates the determination of optimum washing water consumption and optimum duration of washing process for input data as follows:

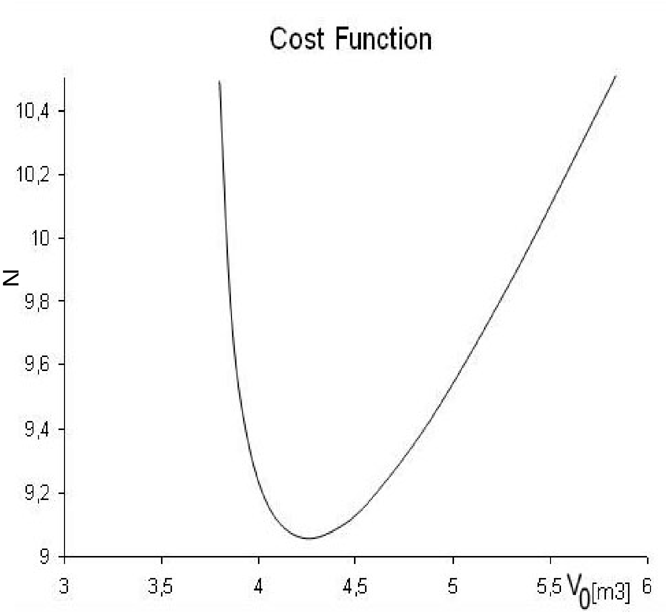

Fig. 4. Cost function

Washing process input data

| | | |
|---|---|---|
| Load of solid phase (washed material) | 5 $m^3 \sim$ 5 t | *[V]* |
| Half-thickness of washed pieces (cured hide) | 2,5 mm | *[b]* |
| Input power of washing drum electric motor | 20kW | *[P]* |
| Required degree of washing process | 0,6 (60%) | *[y]* |
| Specific price of water | 1,5 USD/$m^3$ | *[$K_V$]* |
| Specific price of power | 0,1 USD/kWh | *[$K_E$]* |
| Porosity of solid (washed) phase | 0,5 | *[ε]* |
| Value of effective diffusion coefficient of washed-out component | $10^{-9}$ $m^2$ $s^{-1}$ | *[D]* |

***Optimum results:***

| | |
|---|---|
| Optimum consumption of washing water | 4,3 $m^3$ |
| Operation optimum time | 77,9 min. |
| Optimum cost of washing | 9,06 USD(total *N*),<br>1,81USD$m^{-3}$ (specific *n*) |

## 3 Experimental

The rate constant *k* can be easily determined from equation (2) which integration gives:

$$\ln\left(\frac{a_n}{a_n - a}\right) = k\tau \qquad (11)$$

Plotting natural logarithm $a_n\ (a_n - a)^{-1}$ as a function of time, it is obtained as a straight line whose gradient gives the value of rate constant *k* of dissolution salt. During dissolution of salt, dissociation into $Na^+$ cations and $Cl^-$ anions takes place, making possible the conduction of current. The conductivity of the solution of produced electrolyte is dependent on ionic concentration, charge magnitude of individual ions, on solution temperature and mobility of ions in electric field. For conductivity measurements, the conductivity-meter OK 102/1 with commercial bell electrode Radelkis OK-9023 was employed. The dependence of conductivity on sodium chloride concentration was linear. The solution rate constant was found by measuring changes in conductivity and, thereby, also changes in concentration of salt in solution dependently on time. To stirred distilled water of 120 ml volume tempered at 20°C was suddenly added approximately 4.4g salt. Conductivity measurements were read at 5 s intervals. Experiment results can be seen in Fig. 6 showing the dependence of natural logarithm of difference in concentration of salt on time ($\tau$). The adventitious curve is serving to evaluate the dissolution rate constant *k* according to equation (11).

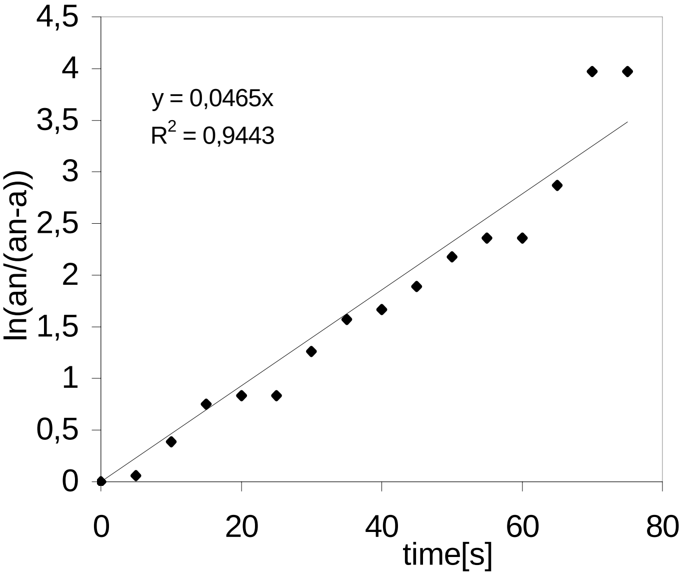

Fig. 5 Determination of rate constant of dissolving (Dependence $\ln(a_n/(a_n - a))$ on time)

The calculated value of rate constant of dissolving is $k = 0{,}0465\ s^{-1}$.

## 4 Discussion

The main aim of our paper was to show, with the use of a relatively simple operation such as the soaking of cured hide, the usefulness and necessity of mathematical simulations for the rationalisation of tanning processes. For its application in specific cases of real operations, it is necessary to insert to the quantitative equations such parameters, which are determined from the measured operation data. In essence, three physical constants – parameters are mentioned: the speed constant of the surface salt dissolving (*k*), the transport parameter (*λ*) and the value of the effective diffusion coefficient of the NaCl ions in the inner volume of the cured hide (*D*). As an example of a practical soaking technology, we have presented the method implemented in a medium-scale tannery in Western Europe. It is obvious that specific technologies in specific places differ from case to case, but indirect modelling, as an effective rationalisation method, can be applied in every tannery, because the critical influence is that of the parameters (*k*, *λ* and *D*), which we have been successful in relatively easily determining. Thus, together with the technological and economical parameters, we are able to determine the optimal duration of the operation and the optimal consumption of technological water. By the term technological water we mean the initial composition of the solution that is used within the individual steps of soaking technology, and the specific (unit) price of which differs from the price of plain water. The results of the simulative calculations of the first step – pre-soak – are shown in the Fig. 1. The shortest time (2, 54 min) and the lowest consumption of technological water (10 $m^3$) are for the speed constant $k=160\ h^{-1}$, which corresponds to the dissolving of plain salt in distilled water; i.e. it is an ideal case. According to our practical measurements from the operation, the speed constant is in most cases ten times lower, i.e. 16 $h^{-1}$, with the optimal time being 16, 8 min, while the consumption of technological water remains almost unchanged (10, 1 $m^3$). If we exceed the optimal time of the operation, then we only increase the electric power consumption costs.

The mathematical model proposed for the soaking operation (see the Eqs. 8 – 8f, 9) enables the rationalisation of the soaking itself, especially the determination of the transport parameter (*λ*), the value of which does not change with swelling and which enables a relatively exact estimation of the time of soaking operation and thereby also the consumption of auxiliary agents (detergents). The modified model enables the determination of the procedure of the soaking operation when there is a risk that the concentration shock causes the collapse of the surface layer texture of cured hide, which can cause complications in further operations. The electron microscopy photographs, interpreted by the experts from FEI, show significant differences in the texture of the cured hide after a slow and rapid desalination of surface layers. The aim of our contribution was not to study the mechanism of desalination, but how to, with the use of indirect modelling, avoid the problems occurring during rapid desalination.

An example of optimization of washing after soaking is presented in the Fig. 5. The dependence of the main operation costs on the consumption of technological water shows a sharp-pointed minimum. Therefore, this case requires very careful control, if we do not want to waste water and electric energy needlessly. Nevertheless, it is necessary to be aware of the fact that the example from Fig. 5 holds true exactly for the input parameters that are stated in the legend below Fig. 5. For specific technologies, the individual data will differ and thereby the location of the optimum will be different as well. Therefore, it is necessary to insert into the mathematical model such technological, economical and physical input data that correspond to the specific conditions of the washing technology and local tannery.

## 4 Conclusion

The presented paper deals with desalination of raw hides, meaning soaking operations with application of a mathematical simulation – indirect modelling – for finding the optimal operation costs. In the whole number of operations through which raw hide is transformed into leather, raw hide desalination is a very important operation in view of final quality. The incorrectly performed procedure may cause extensive damage to border parts of raw hide and consequently considerable economic losses in final production of leather substance. To avoid the above-mentioned economical losses, we applied indirect modelling, too. Both these examples give us advantages and benefits of the mathematical simulation approach to the rationalization of tanning processes.

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*List of symbol:*

| | | | |
|---|---|---|---|
| $P$ | - | electric motor input power | [kW] |
| $K_E$ | - | unit price of power | [USD/ kWh] |
| $V$ | - | volume of technological water | [m$^3$] |
| $K_V$ | - | unit price of technological water | [USD/m$^3$] |
| $\tau$ | - | time | |
| $a$ | - | mass fraction of salt in technological water | |
| $a_n$ | - | mass fraction of salt in technological water corresponding to concentration of saturated solution at given temperature | [l] |
| $a_p$ | - | surface mass fraction of salt related to mass of raw hide at start of desalination process ($\tau = 0$) | [l] |
| $N_a$ | - | soaking number | [1] |
| $k$ | - | dissolving rate constant of surface salt | [h$^{-1}$] |
| $m_v$ | - | mass of technological water | [kg] |
| $m_s$ | - | mass of cured hide | [kg] |
| $\rho_v$ | - | density of technological solution | [kg m$^{-3}$] |
| $\rho_s$ | - | density of cured hide | [kg m$^{-3}$] |
| $V_s$ | - | volume of cured hide | [m$^3$] |
| $y$ | - | required cured hide desalination degree or coordinate | [l] |
| $x$ | - | coordinate | [m] |
| $c$ | - | volume concentration NaCl in cured hide | [kg m$^{-3}$] |
| $c_0$ | - | volume concentration NaCl in drum bath | [kg m$^{-3}$] |
| $D$ | - | effective diffusion coefficient NaCl in cured hide | [m$^2$s$^{-1}$] |
| $S$ | - | outer surface of cured hide | [m$^2$] |
| $b$ | - | half thickness of cured hide | [m] |

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