

OPTIMIZATION OF RAW HIDE CURING USING TWO-COMPONENT COUNTER-CURRENT DIFFUSION MODEL*

by

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ABSTRACT

Curing with concentrated brine solution (sodium chloride) is a common method for raw hide preservation. Sodium and chloride ions diffuse towards the raw hide inner volume, which initiates the counter-current transport of water from the raw hide inner volume. The result of the two-component counter-current diffusion is increasing salt content and decreasing water content in the raw hide inner volume. For optimization of the curing process it is necessary to determine the time dependence of the brine concentration from the hide surface towards its center, it means the non-stationary concentration field in the inner volume of the hide. For this reason we have proposed a mathematical-physical model for NaCl diffusion in the hide. We have also carried out the numerical solution of the model; the solution comprises the concentration fields of sodium chloride and water during the curing process. The respective effective diffusion coefficients and their dependence on brine concentration have been determined experimentally. The result of the mathematical simulation and mathematical evaluation of the experimental data was estimation of the optimal time for raw hide curing at the given boundary conditions, and a sufficient brine concentration in the inner volume of the hide.

RESUMEN

El curado con una solución de salmuera concentrada (cloruro de sodio) es un método común para la preservación de cuero crudo. Los iones de sodio y cloruro se difunden hacia el volumen interior del cuero crudo, el cual inicia el transporte en contracorriente de agua desde el interior del cuero crudo. El resultado de la difusión en contracorriente de los dos componentes es aumentar el contenido de sal y disminuir el contenido de agua en el volumen interior del cuero crudo. Para la optimización del proceso de curado es necesario determinar la dependencia del tiempo en la concentración de salmuera desde la superficie de la piel hacia su centro, es decir el gradiente de concentración móvil en el volumen interno de la piel. Por esta razón, hemos propuesto un modelo físico-matemático para la difusión de NaCl en la piel. También hemos llevado a cabo la solución numérica del modelo; la solución incluye los gradientes de concentración de cloruro de sodio y agua durante el proceso de curado. Los respectivos coeficientes de difusión efectiva y su dependencia de la concentración de salmuera se han determinado experimentalmente. El resultado de la simulación matemática y la evaluación matemática de los datos experimentales fue la estimación del momento óptimo para el cuero crudo curado en condiciones límites, y una concentración de salmuera suficiente en el volumen interno de la piel.

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INTRODUCTION

Fresh hides have to be processed in tanneries within a few hours after flaying¹ to protect the hides from decay. In most cases, this is logistically impossible and the hides have to be preserved before transportation. Generally, there are two ways of preservation — short-term preservation (in days) that includes icing, refrigeration, or chemical preservation such as antiseptics and biocides, and long-term preservation which lasts for months and includes for example drying or brine-curing.

Curing with common salt (sodium chloride, NaCl) is the most widespread method of long-term raw hide preservation in Europe and America. At moderate temperatures, salt-preserved hides can be kept for up to 1 year.¹ The use of crystalline NaCl is more common in Europe, while in the United States the most prevalent method is brine curing with saturated solution of NaCl.² Preservation with sodium chloride is advantageous from several points of view — it is relatively easy, cheap and suitable for both continental and intercontinental transportation. Still, there are many disadvantages. One of them is that the brine-cured hides are susceptible to halophilic bacteria growing in the saturated salt environment (causing so-called “red heat”).^{1,3} Other problem of brine curing is corrosion and other transportation difficulties, and the most serious and disputed issue is the negative impact on the environment as it burdens the environment with large amounts of total dissolved solids (TDS).⁴

For these reasons, alternatives of brine curing have been intensively investigated. One of them is chemical preservation with antimicrobial and fungicidal substances such as sodium sulfite with acetic acid,⁵ saturated boric acid,⁶ commercial substances on the basis of dimethyldithiocarbamate and isothiazoline⁷ and 2-thiocyanomethylthiobenzothiazol (TCMTB),⁸ a powder agent Lircure (containing EDTA, NaCl and wood saw-dust)⁹ used in South Africa or a biocide substance Proxel X¹⁰ in combination with boric acid, which is according to¹ the best alternative of temporary preservation of fresh hides. Another chemical alternative is the replacement of NaCl with potassium chloride (KCl).¹¹ Very promising and environmentally friendly method of preservation is irradiation, for example electron beam irradiation described in reference¹². Light skins can be also preserved by pickling,^{1,2} usually in 10% solution of NaCl with 1% H₂SO₄, and chrome tanning¹ has been used to preserve cattle hides. The latter method decreases the salt burden in waste water and leads to a raw product called wet-blue, which can be further treated with fungicides or other preservation agents. In his comprehensive work¹ Bailey also describes the possibility of bio-preservation of raw hides with the use of anti-bacterial peptides (“bacitracins”) produced by microorganisms.

Simultaneously with the R&D of raw hide preservation methods alternative to brine curing, a close attention is also paid to brine curing itself as it is still the most widespread method of long-term raw hide preservation. The joint aim of all attempts is to decrease the amount of salt used in the curing process. One of the possibility can be partial replacement of NaCl with other chemicals such as superabsorbent (co)polymers (SAP),¹³ a combination of NaCl with p-chloro-meta-cresol after previous dehydration of the hides or with sodium meta-bisulphate,^{14,15} or the use of hide curing additives such as essential oils with antibacterial properties in combination with non-ionic surfactants which enhance the diffusion of NaCl into the hides and makes the brine curing process more efficient.¹⁶ Another possibility is the salt recovery from the effluents after soaking or curing and its re-use in the curing process.⁴

A new approach to the curing process lies in the use of theoretical tools of chemical engineering. In our contribution we are dealing with optimization of raw hide preservation by saturated brine solution on the basis of mathematical simulation. This paper follows from the work¹⁷ where the concentration field and time concentration of NaCl in brine solution were modeled in dependence on the ratio of the volumes of brine solution and cured hide (soaking number – Na). The minimal time needed for sufficient salting of raw hides is given by high values of the concentration gradient at the surface which is maximal at high Na. This leads to electric power savings, but at the same time to a significant consumption of brine solution. However, the maximal value of the concentration gradient at the surface can be also achieved with the use of the mixture of saturated brine solution with solid NaCl. The addition of solid NaCl is selected in order to achieve only saturated brine solution at the end of the curing process; in other words, all the solid sodium chloride is spent on raw hide curing.

THEORY

The mathematical model of raw hide preservation proceeds from the continuous reaction model.¹⁸ As well as in model reference,¹⁷ we assume a progressive salt diffusion into the inner hide volume and forming of non-stationary concentration field (Figure 1).

The exact quantitative model is given by mathematical description of two-component counter-flow diffusion of NaCl and water. The model is represented by a series of partial differential equations, the detailed description and numerical solution of which are currently under preparation. In this paper, the entire complexity of the real transport process is included in the value of the effective diffusion coefficient (D_{ef}) of NaCl ions in the inner volume of cured hide similarly as it is described in the referenced work.¹⁷ The

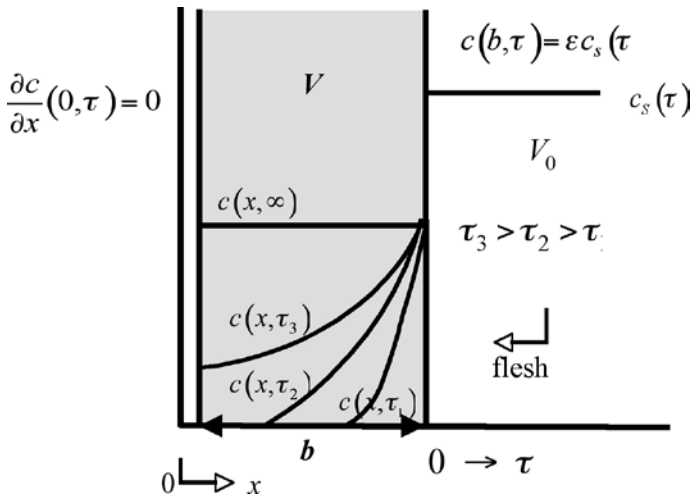


Figure 1. – Mathematical model of NaCl diffusion into the inner volume of raw hide during the brine curing process.

value of D_{ef} depends particularly on concentration and due to the non-stationary concentration field also on time. If these dependences were significant, the advantage of introducing the effective value might be lost. For this reason we were dealing with the dependence of D_{ef} on NaCl concentration, which was determined experimentally for brine solutions of various NaCl concentrations in porous environment represented by filtration paper (cellulose).

Mathematical model of raw hide curing at constant surface gradient of NaCl concentration

The results from the experimental determination of the dependence of the effective diffusion coefficient (D_{ef}) on NaCl concentration in brine solution (see below in the Experimental part) showed that this dependence was not significant; therefore for practical purpose we can use its integral average value. With this assumption, the quantitative model of raw hide curing is as follows:

$$\frac{\partial c}{\partial \tau}(x, \tau) = D \frac{\partial^2 c}{\partial x^2}(x, \tau) \quad 0 < x < b \quad \tau > 0 \quad (1)$$

$$\frac{\partial c}{\partial x}(0, \tau) = 0 \quad (2a)$$

$$c(b, \tau) = \epsilon c_s \quad (2b)$$

$$c(x, 0) = 0 \quad (2c)$$

$$\frac{\partial c}{\partial x}(0, \tau) = 0 \quad (2d)$$

In our contribution, we assume that NaCl concentration (c_s) of the brine solution surrounding the cured hide as well as the ratio between the volumes of the solid and liquid phases remain constant during the whole curing process. This simplifies the mathematical model published in.¹⁷ To find the solution for the model it is easier to introduce the following dimensionless parameters:

$$C = \frac{c}{\epsilon c_s} \quad (3a)$$

$$X = \frac{x}{b} \quad (3b)$$

$$Fo = \frac{D\tau}{b^2} \quad (3c)$$

$$C(1, Fo) = 1 \quad (3d)$$

$$\frac{\partial C}{\partial X}(0, Fo) = 0 \quad (3e)$$

$$C(X, 0) = 0 \quad (3f)$$

After application of Laplace transformation, the following analytical solution was obtained:

$$C = 1 - \sum_{n=1}^{\infty} \frac{\cos \left[X (2n-1) \frac{\pi}{2} \right] e^{-\frac{Fo(2n-1)^2 \pi^2}{4}}}{(2n-1)\pi (-1)^{n+1}} \quad (4)$$

The dimensionless sodium chloride concentration field within the hide is shown in Figure 2:

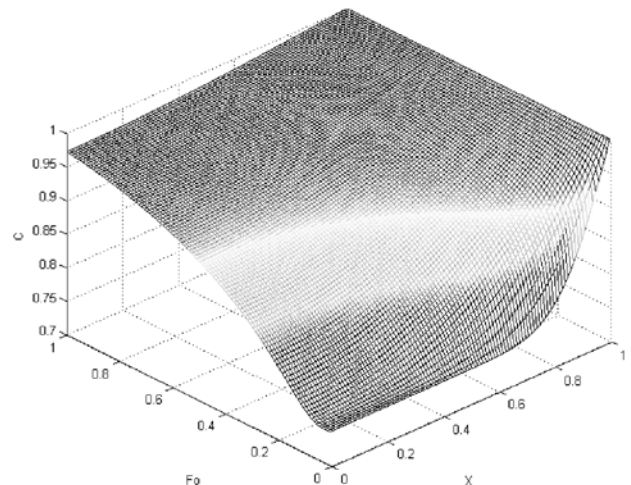


Figure 2. – Dimensionless sodium chloride concentration field within the hide during the curing process.

The integral average concentration is represented by Eq. (5):

$$\bar{C} = \int_0^1 C(X, Fo) dX \quad (5)$$

After integration, we get:

$$\bar{C} = 1 - 2 \sum_{n=1}^{\infty} \frac{(-1)^{2n+3} e^{-\frac{Fo(2n-1)^2 \pi^2}{4}}}{(2n-1)^2 \pi^2} \quad (6)$$

The time dependence of the integral average concentration is shown in Figure 3:

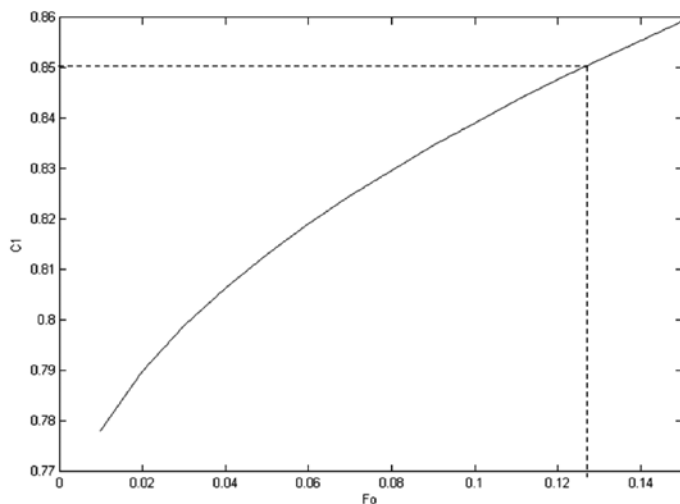


Figure 3. – Dimensionless sodium chloride concentration field in the hide during the brine curing process.

Determination of the effective diffusion coefficient and its dependence on concentration

The value of the diffusion coefficient at infinite dilution can be calculated by means of the Nernst-Haskell equation.¹⁹

$$D_0 = \frac{RT}{F^2} \left(\frac{l_+^0 l_-^0}{l_+^0 + l_-^0} \right) \left(\frac{z_+ + z_-}{z_+ z_-} \right) \quad (7)$$

where D_0 [$\text{cm}^2 \text{s}^{-1}$] is the diffusion coefficient at infinite dilution, R [$\text{J mol}^{-1} \text{K}^{-1}$] is the universal gas constant, F [C mol^{-1}] is the Faraday constant, l_+^0, l_-^0 [$\text{S cm}^2 \text{mol}^{-1}$] are limiting ionic conductances for cations and anions, respectively, T [K] is the absolute temperature, z_+, z_- [1] are the valences of cations and anions, respectively.

The value of the diffusion coefficient at infinite dilution for NaCl is $1.58 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

The value of the effective diffusion coefficient of NaCl in the hide is obtained from the experimental data. The concentration of NaCl decreases with time from its source, i.e. the initial concentration. In an adequate distance, the NaCl concentration is practically zero. However, this critical distance (a) increases with time and its time speed is proportional to the diffusion flux of NaCl. The physical interpretation proceeds from the mass balance:

$$Sc_p \frac{da}{d\tau} = SD_{ef} \frac{(c_p - c_{min})}{a} \quad (8)$$

Assuming that $c_{min} \ll c_p$, we get:

$$\frac{da}{d\tau} = \frac{D_{ef}}{a} \quad (9)$$

where D_{ef} is the effective diffusion coefficient [$\text{m}^2 \text{s}^{-1}$], τ is the time [s] and a represents the radius obtained from the experimental data [m]. After integration and rearrangement of Eq. (9), we get

$$a = \sqrt{2D_{ef}\tau} \quad (10)$$

where $\sqrt{2D_{ef}} = k$ and k denotes the slope of the straight line. The diffusion coefficient is then easily calculated according to the following equation:

$$D = \frac{k^2}{2} \quad (11)$$

The question remained how to identify the minimal concentration. We proceeded from the chloride determination by method of Mohr.²⁰ The determination of the equivalent amount of silver nitrate (AgNO_3) is given by the different value of the solubility product. At the equivalence point, the corresponding concentration of chloride ions is approximately 10^{-5} (according to the value of solubility product of AgCl).²¹ As soon as the AgNO_3 concentration exceeds this concentration, a red precipitate of silver chromate (bichromate) begins to appear, the necessary concentration of which is approximately 10^{-4} . In practice it means that in the areas with no NaCl we get reddish-brown color (in case of using sodium or potassium chromate or bichromate), while the areas containing NaCl are white (white precipitate of AgCl). This color boundary changes in time and is used for determination of the effective diffusion coefficient of NaCl in the hide. A different situation occurs when using

sodium sulphide (Na_2S) for color indication. Due to the fact that the solubility product of Na_2S is 6×10^{-51} ,²¹ the precipitate is formed both in NaCl containing and NaCl free areas. The resulting color of the area containing NaCl is grey, while the outside area (with no NaCl) is dark brown. According to our experiments, also this color boundary can be visually identified.

EXPERIMENTAL

Color indication of NaCl diffusion in cellulose

0.05 ml of NaCl aqueous solution of different concentrations (1%, 5%, 10%, 15%, 20%, 26% and 30% (w/v)) was applied onto a wetted filtration paper by a micropipette. The paper was placed in a Büchner funnel, the bottom part of which was situated in an Erlenmeyer flask half-filled with water to keep the filtration paper constantly wetted and to prevent the diffusion process from stopping. The diffusion of sodium chloride was monitored for each concentration in the following times (in minutes): 5, 15, 30, 60, 90, 120, 240, 360, 600, 960 and 1140. After the selected time period, the paper was sprayed over with 1% (w/v) AgNO_3 , the reaction giving white precipitate of silver chloride (AgCl), and consequently the paper was sprayed over with 1% (w/v) sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or 1% (w/v) sodium sulphide (Na_2S). The color boundary was identified visually and marked. Photographs of the individual papers were taken (see Figure 4a,b). The pictures were processed with the use of Adobe Photoshop CS3 Extended 10.0 equipped with a technical image analysis tool in order to determine the areas containing NaCl . The measured areas were considered to possess a circle shape; therefore the radiuses were obtained using the equation for the area of a circle.

Determination of the effective diffusion coefficient of NaCl in cellulose

At first, the time dependences of the radiuses obtained from the above described experiment were made on the square root of time for the individual concentrations. Linear regression was applied to get the slopes of the straight lines (see Figure 5).

The resulting values of the effective diffusion coefficient of NaCl in cellulose calculated according to Eq. (11) are shown in Table 1.

Color indication of NaCl diffusion in raw hide

The method of color indication of sodium chloride with the use of Na_2S was tested on fresh animal hides. Raw cow hides and pig skins were provided by the abattoir Jacom, spol. s.r.o., Holešov, Czech Republic. The hides were immediately cut into pieces of approximately 5×5 cm and put into brine solution of the salt concentration of 30% (w/v) for various time periods. The hides were then briefly rinsed in clear

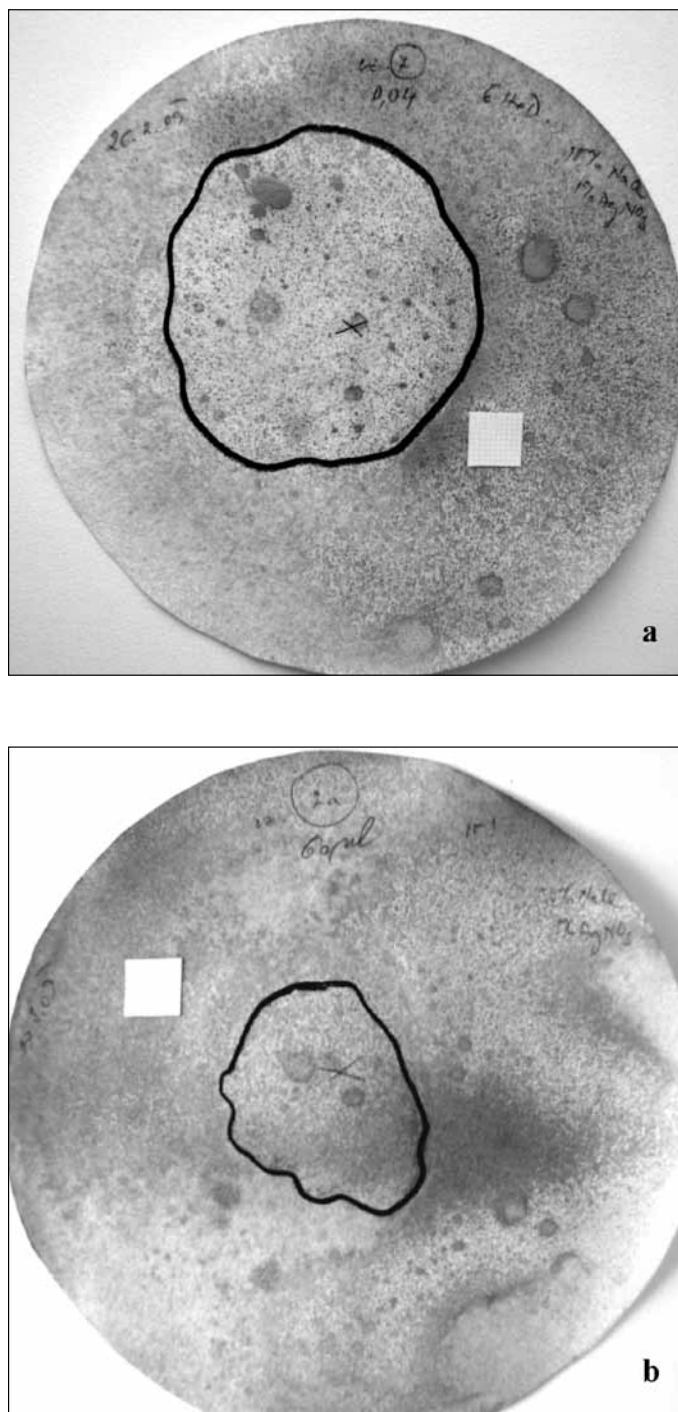


Figure 4. – Examples of the results of color identification of NaCl on cellulose (filtration paper) with the use of Na_2S : a) 15% NaCl (w/v), time 360 min; b) 30% NaCl (w/v), time 15 min.

water and cut manually with a trapezoidal-blade knife (from the flesh side towards the grain). The exposed cross-section were sprayed over with 1% (w/v) AgNO_3 and consequently with 1% (w/v) solution of Na_2S . The color boundary was photographed with the use of Olympus SZX7 microscope equipped with Olympus KL 1500 LCD light equipment and Olympus C-5060 digital camera.

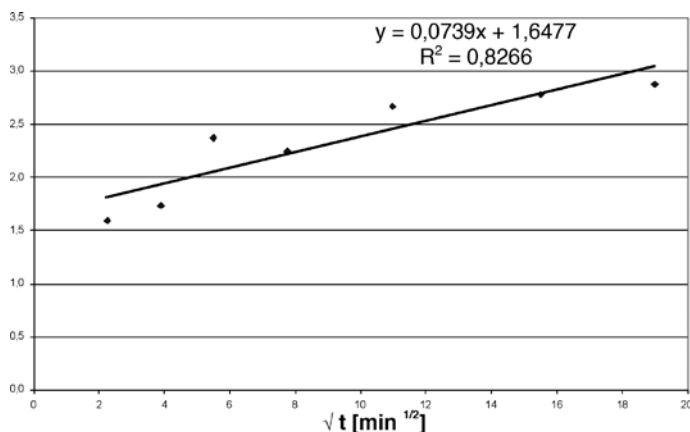


Figure 5. – Determination of the effective diffusion coefficient of NaCl in cellulose from the slope of the straight line. The graph corresponds to the initial NaCl concentration of 20% (w/v).

TABLE I

Experimental determination of diffusion coefficient of NaCl

NaCl concentration [% w/v]	Effective diffusion coefficient [$\times 10^{-9} \text{ m}^2\text{s}^{-1}$]
1	1.56
5	2.73
10	5.81
15	6.04
20	4.55
26	6.54
30	4.00

DISCUSSION

The values of the effective diffusion coefficient (D_{ef}) dependent on NaCl concentration, which were evaluated on the basis of NaCl diffusion in cellulose, varied from $1.56 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ to $6.54 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ in the range of the initial NaCl concentration 5-30% w/v (see Table 1). In addition, the effective diffusion coefficients obtained from the experimental data are of the same order of magnitude as the theoretical value calculated for infinite dilution from Eq. (8). These facts enable us to use the integral average value of D_{ef} in the presented mathematical model of raw hide curing for optimization of the operating time.

There is no reference in the literature to visual detection of NaCl diffusion in materials except of the work¹⁷ in which epifluorescence microscopy method was used for sodium ions identification on a raw hide cross section. Our aim was to develop a quick and relatively cheap method by which it would be possible to approximately detect the progress of NaCl diffusion in raw hide by the naked eye or a light microscope. The method was at first tested on filtration paper (cellulose) and then on raw hide with the use of Na_2S or $\text{Na}_2\text{Cr}_4\text{O}_7$ as indicators. The results showed that both indicators were suitable in the case of filtration paper, but only Na_2S worked well in the case of raw hide where it created visible color boundary. The preliminary results are shown in the following Figure 6 (a-d).

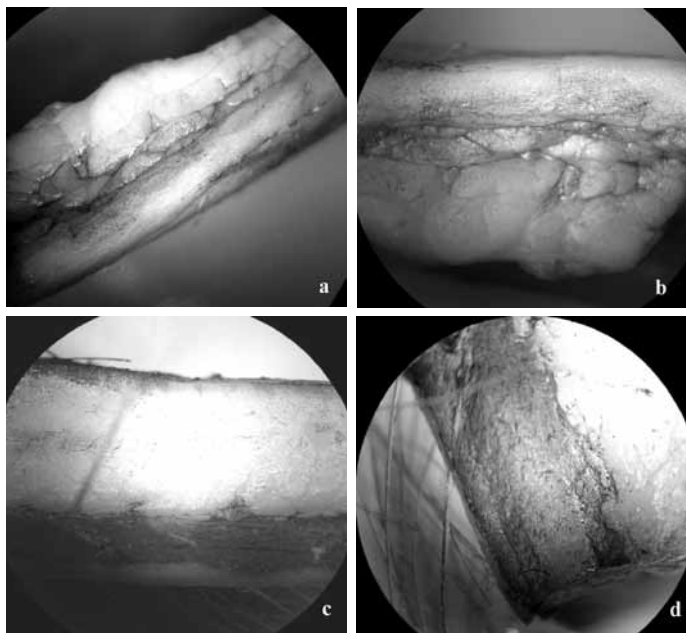


Figure 6. – Color boundary in hides cured with 30% (w/v) NaCl – the areas with diffused NaCl are bright, dark areas signify the absence of NaCl. a, b – Pig skin, time: 24 h; c, d – Cow hide, time: 16h.

In addition, the use of Na_2S is suitable also from the safety and health protection reasons, because chromates and bichromates are highly toxic and carcinogenic. It can be seen from Figure 6 that sodium chloride diffuses first through the fat layer and in the hide the process significantly slows down. The figures also imply the possibility that NaCl diffusion in the hide takes place from both the flesh and the grain side. This would mean more precise evaluation of the used mathematical model. We will continue with the improvement of the quantitative description of the curing process and more extensive experiments are planned to make the used method more reliable and precise enough to enable the calculation of the effective diffusion coefficient in similar way as it was in the case of filtration paper. A considerable problem of this method is that the hide is greasy, so it repels water and the color boundary can be partly washed out from

the surface of the hide cross-section. One way how to eliminate this problem is a surface treatment of the hide cross section with a substance that would decrease the water-repellent properties of the hide. The inner hide texture may also play an important role.

For the determination of the optimal time we proceed from Figure 2, which represents the dependence of the integral average value of the dimensionless sodium chloride concentration in the inner volume of the cured hide on the dimensionless time (Fourier's diffusion criterion, Fo). For example, at 85% saturation of the hide the corresponding dimensionless time is 0.125. At the value of the effective diffusion coefficient $D_{ef} = 4.52 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and the thickness of the cured hide $b = 0.5, 1.0$ and 1.5 cm , the estimated time of the proper curing will be 0.19, 0.75 and 1.66 h respectively. It follows that the time is square-proportional to the hide thickness. For comparison, to achieve 85% saturation of the cured hide at Na (soaking number) = 3, the dimensionless time is approximately 1.8.¹⁷ It means that if we used a brine solution of the initial NaCl concentration equal to saturation (approx. 30% w/v), we would have to use the minimal Na of 3 and the respective times calculated in our case for constantly saturated brine solution (a blend of saturated NaCl solution + solid NaCl) would have to be multiplied by the ratio of $1.8/0.125 = 14.4$. In addition, the consumption of water is considerably lower in our case. This is considered to be the most significant practical result of the presented work.

CONCLUSIONS

Curing with concentrated brine solution (sodium chloride) is one of the most widespread methods for raw hide preservation. For optimization of the curing process it is necessary to determine the time dependence of the brine concentration from the hide surface towards its center, it means the non-stationary concentration field in the inner volume of the hide. In our contribution, a mathematical-physical model of NaCl diffusion has been proposed for determination of the optimal curing time at the NaCl concentration corresponding to saturated brine solution. This is achieved by a blend of NaCl solution and solid NaCl. The solution of the model comprises the concentration fields of sodium chloride and water during the curing process. The results show that with this approach it is possible to considerably decrease the time necessary for proper curing as well as water consumption. The respective effective diffusion coefficients and their dependence on brine concentration have been determined experimentally on cellulose (filtration paper) and compared to the diffusion coefficient of NaCl calculated at infinite dilution. A method of visual identification of NaCl diffusion with the use of Na_2S has been introduced. The method works well on

cellulose and the preliminary tests have also shown promising results on cured hide. More extensive elaboration of the identification method is planned for precise determination of the effective diffusion coefficient of NaCl in the hide.

LIST OF SYMBOLS

$ a $	Distance of salinization boundary	[m]
$ b $	Raw hide thickness	[m]
$ c $	Concentration of NaCl in cured hide	[kg m ⁻³]
$ c_{min} $	Concentration of NaCl in cured hide at salinization boundary	[kg m ⁻³]
$ c_p $	Initial concentration of NaCl in filtration paper	[kg m ⁻³]
$ c_s $	Concentration of NaCl in saturated brine solution	[kg m ⁻³]
$ D $	Diffusion coefficient of NaCl in cured hide	[m ² s ⁻¹]
$ D_{ef} $	Effective diffusion coefficient of NaCl in cured hide	[m ² s ⁻¹]
$ \bar{C} $	Integral average concentration	[1]
$ S $	Area of NaCl transport	[m ²]
$ V $	Volume of the cured hide	[m ³]
$ V_0 $	Volume of the brine solution	[m ³]
$ x $	Coordinate	[m]
Greek symbols		
$ \varepsilon $	Porosity	[1]
$ \tau $	Time	[s]

Other symbols are explained directly in the text.

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