Relationship between mass transport and the quality of bio-materials

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Abstract: - The advantages of one-dimensional mathematical simulations of the process of raw hide desalination are presented. A general three-dimensional model is to be considered in our following contribution. Technological data, i.e. transport parameter and effective diffusion coefficient of salt in cured hide, were determined experimentally. A possible occurrence of a concentration shock is modelled, and a method of its prevention is proposed to reduce losses in the hide substance.

Key words:- Soaking, diffusion, concentration shock, one-dimensional model.

1 Introduction

Leather belongs to the category of products which we are in daily contact with and which are made of biological material. Raw hide of slaughter and game animals is the principle raw material for leather, which is further processed in leather manufacturing, shoemaking, haberdashery, textile industry, etc. The process of transformation of raw hide into leather consists of approximately 30 chemical, physical and mechanical operations. The processing of 1.000 kg of raw hide into leather results in creating 200 kg of leather with chromium content of 2.8 kg, 350 kg of non-tanned protein waste and 250 kg of tanned wastes with chromium content of 3.5 kg, and the tanning process gives up to 100,000 kg of waste water containing 10 kg of chromium. Consequently, only 20% of the proteinaceous collagen raw material is valorized by leather manufacturing processes and 74% of chromium ends as waste. Heavy losses of collagen mass and a considerable consumption of electric energy, technological water, leather manufacturing chemicals and heat have made leather chemists to the attempts at rationalization and optimization of the raw hide processing.

Mathematical simulations, commonly used in chemical industry as a main tool of chemical engineering, are only very slowly promoted in leather industry. Besides historical reasons – mainly handicraft of leather – the application of theoretical tools of chemical engineering is complicated by the relatively complex structure and texture of collagen solid phase. Progressing concentration of leather production and increasing requirements for environmental protection have caused, besides conventional methods of leather manufacturing research based mainly on experimental work, that quantitative approaches are also starting to come in. It considers mostly the use of mathematical statistics in mass data processing and determining the factors with dominant effects on the quality of the final product – leather. The second quantitative approach studies the chemical-physical mechanisms of the processes of raw hide transformation into leather. In this case, the theory of chemical kinetics of heterogeneous reactions and the reactor engineering are used. The main equipment, in which most of the chemical-physical transformations of raw hide into leather take place, is the tanning drum, which represents, from the chemical engineering point of view, a non-isotherm and non-adiabatic reactor. Our contribution uses the last mentioned method and applies a "continual reaction" model to optimize the process of raw hide soaking.

The raw hide coming to tanneries is preserved in most cases by sodium chloride, the content of which in the hide ranges between 30-40%. The salt used for preservation is then removed by washing the hide in specially modified soak liquor. While the elimination of the solid salt on the surface does not represent any special problem, the elimination of an almost saturated salt solution from the inner volume of the hide is accompanied by considerable concentration changes and by changes of osmotic pressure. These changes lead to heavy damage of fine hide surface layers and consequently to considerable economic losses represented by the losses of hide substance. In our contribution, a mathematical description of the soaking operation is presented and a controlling algorithm proposed that reduces the damage of the fibrous structure to the minimum. The theoretical conclusions are supported by experimental measurements based on the use of electron microscopy.

2 Theory

Consider a raw hide sample placed in a basin of surrounding liquor. The sample has usually the shape of a long sheet with two of its dimensions considerably greater then the thickness. Denote by *2b* the thickness of the sheet and assume that it is possible to restrict ourselves to modeling the soaking procedure in the direction of the cross-section. This means that we neglect concentration gradients in the remaining two directions. Denote by $c(x,\tau)$ the concentration of salt in the sample at point x (x varies from $-b$ to $+b$) and time τ ($\tau > 0$). The surrounding liquor is well stirred and thus the concentration of salt here is considered to be a function of time only. Thus, $c_0(\tau)$ denotes the concentration of salt in the surrounding liquid at the time τ. The process of raw hide soaking is modeled by the system of equations (1)—(6) and the Figure1:

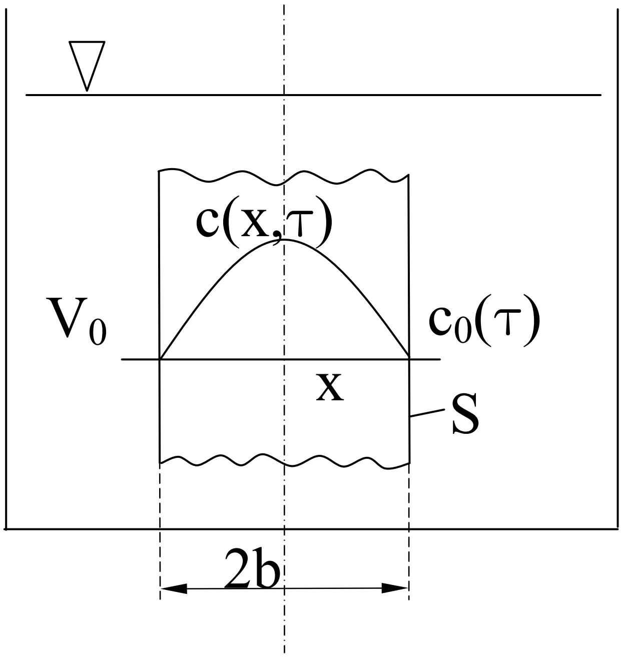

Fig.1. Model of soaking.

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

$$-DS\frac{\partial c}{\partial x}(b,\tau) = V_0\frac{dc_0}{d\tau}(\tau) \quad (2)$$

$$c(b,\tau) = \varepsilon c_0(\tau) \quad (3)$$

$$\frac{\partial c}{\partial x}(0,\tau) = 0 \quad (4)$$

$$c(x,0) = c_p \quad (5)$$

$$c_0(0) = 0 \quad (6)$$

Here D denotes the diffusion coefficient in the sample, S denotes the area of the sample, V_0 the volume of the surrounding liquid and ε the porosity of the sample.
Let us introduce the following dimensionless quantities

$$X = \frac{x}{b};\qquad Fo = \frac{D\tau}{b^2};\qquad Na = \frac{V_0}{Sb};$$

$$C(X,Fo) = \frac{c(x,\tau)}{c_p};\qquad C_0(Fo) = \frac{\varepsilon c_0(\tau)}{c_p}$$

Equations (1) – (6) are then transformed to

$$\frac{\partial^2 C}{\partial X^2}(X,Fo) = \frac{\partial C}{\partial Fo}(X,Fo),\ 0<X<1,\ Fo>0 \quad (7)$$

$$-\frac{\partial C}{\partial X}(1,Fo) = \frac{Na}{\varepsilon}\frac{dC_0}{dFo}(Fo) \quad (8)$$

$$C(1,Fo) = C_0(Fo) \quad (9)$$

$$\frac{\partial C}{\partial X}(0,Fo) = 0 \quad (10)$$

$$C(X,0) = 1 \quad (11)$$

$$C_0(0) = 0 \quad (12)$$

After solving the system (7)–(12), we receive

$$C = \frac{\varepsilon}{\varepsilon+Na} + 2Na\sum_{n=1}^{\infty}\frac{\cos(Xg_n)\exp(-Fo\cdot g_n^2)}{Na\, g_n \sin(g_n) - (Na+\varepsilon)\cos(g_n)} \quad (13)$$

where g_n are roots of the equation:

$$tg(g) = -\frac{g\, Na}{\varepsilon} \quad (14)$$

The concentration field is shown in Figure 2 in the range of dimensionless times $0.05 \le F_0 \le 1$, the evolution of the dimensionless concentration in the surface layer ($X = 0.1$) is shown in Figure 3.

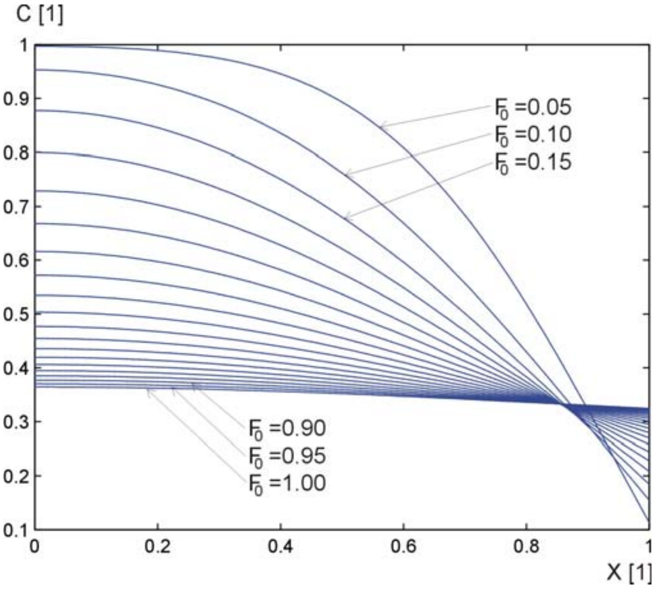

Fig. 2. Concentration field in cured hide.

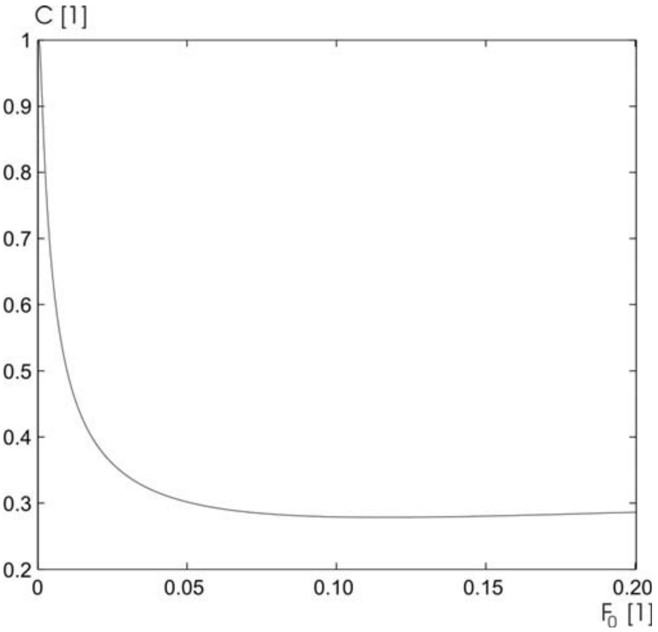

Fig. 3. Concentration of salt in the surface layer in dependence on dimensionless time.

Both the figures, especially Figure 3, show significant concentration changes in a very short time interval (concentration shock), which can cause damage to the fine fibrous hide structure. To eliminate this risk, we suggest the following procedure: after dissolving the surface salt, the bath in the tanning drum contains practically saturated solution of salt, which we do not drain. Instead, we bring into the drum a very small inflow of the soak liquor and at the same time we let the salt solution flow out of the drum at the same rate.

3 Experimental

During the transport of salt, dissociated ions Na^+ and Cl^- cause a change in electric conductivity of the solution. The conductivity of the salt solution depends on ionic concentration and we choose the linear part of the calibration curves.

The conductivity-meter OK.102/1 with commercial electrode Radelkis OK-9093 was used.

As mentioned before, the soaking process is represented by the model described by equations (1)—(6).

For determination of the effective diffusion coefficient we used the following equation (Crank and Park, 1968).

$$\frac{m(\tau)}{m(\infty)} = \left(1+\alpha\right)\left(1-\exp\left(\frac{D\tau}{b^2\alpha^2}\right)erfc\left(\frac{D\tau}{b^2\alpha^2}\right)\right) \quad (15)$$

$$\alpha = \frac{V_0}{V} = \frac{Na}{\varepsilon} \quad (16)$$

where *m(τ)* [kg] is the mass of sodium chloride transferred from the hide into the bath during the time *τ*, *m(∞)* [kg] is the total mass of sodium chloride to be transferred from the hide into the bath before the system reaches equilibrium, *α* is a dimensionless soaking parameter defined by (16) and *erfc* is the complementary error function.

Let us introduce the parameter *λ* by

$$\lambda = \frac{D}{a^2} \quad (17)$$

where D [m^2s^{-1}] is the diffusion coefficient of sodium chloride in water at low concentrations and a [m], where a is the pore half length.

For small times, it is possible to write the relationship (26) by the Taylor series expansion and neglect the higher order terms to obtain

$$\frac{m(\tau)}{m(\infty)} = \frac{2}{\sqrt{\pi}}\frac{1+\alpha}{\alpha}\sqrt{\lambda\tau} \quad (18)$$

It follows from the equation (18) that the dependence of *m(τ)/m(∞)* on the square root of *τ* is linear, as long as the assumptions of the model are valid. Taking into account the results (Blaha and Kolomazník, 1989) and the accuracy of our measurements, we may conclude that the linear dependence holds approximately for values of $m(\tau)/m(\infty)$ less than 0.6. Thereafter, the experimental values should be located under the straight line with increasing time.

Figure 6 represents a typical example for low dry matter content.

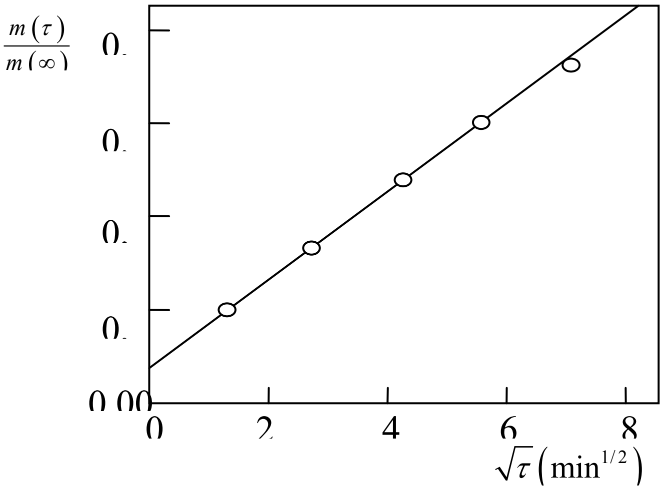

Figure 6. The initial phase of salt removal.

Transport coefficient λ can be calculated from equation (18) as follows

$$\lambda = \frac{k^2\pi}{4}\left(\frac{\alpha}{1+\alpha}\right)^2 \qquad (19)$$

where k is the slope in the relationship (18).

Experimental values:
$a = b = 5$ mm (during the experiment, swelling does not take place)
$\frac{\alpha}{\alpha+1} = 1$,
$k = 0.1 \text{ min}^{-½}$,
$\lambda = 7.85 \times 10^{-3} \text{ min}^{-1} = 1.3 \times 10^{-4} \text{ s}^{-1}$,
$D = 3.25 \times 10^{-9} \text{ m}^2\text{s}^{-1}$

4 Discussion

The main aim of our paper was to show, through the example of a relatively simple operation such as cured hide soaking, the usefulness and necessity of mathematical simulations for the rationalisation of tanning processes. To apply mathematical simulations in specific cases, it is necessary to measure certain parameters, which are then inserted to the quantitative equations. In essence, two physical parameters are present: the transport parameter (λ) and the effective diffusion coefficient (D) of the NaCl ions in the inner volume of cured hide. The mathematical model proposed for the soaking operation (see equations (1)—(6)) 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 and thereby also the consumption of auxiliary agents (detergents). The through-flow soaking model enables us to determine how the soaking operation should be carried out when there is a risk that the surface layer texture of cured hide collapses in consequence of the concentration shock, which can lead to complications during further operations.

Our contribution shows how to avoid, with the help of a mathematical simulation, the problems of the damage of fine surface structure of cured hide that might occur during rapid desalination.

Both the mathematical models representing the one-dimensional cases are linear and very simple, which enables us to find the corresponding analytical solutions. In real industrial practice, this is often not the case and we deal with a general three-dimensional model, where the thickness of hide depends on the position. In our following paper*, we deal with such a general setting and we show that the conclusions introduced in this paper can be generalized.

5 Conclusions

The present paper deals with desalination of raw hides (i.e. soaking operations) from the point of view of the application of mathematical simulations for the optimal technology proposal. In the whole number of operations through which raw hide is transformed into leather, desalination is a very important operation in view of the final quality. Incorrectly performed desalination procedure may cause extensive damage to border parts of raw hide and consequently considerable economic losses in the final production of leather substance. To avoid these losses, we proposed a new technology based (among others) on mathematical simulations. Both the presented examples show the advantages and benefits of the mathematical simulation approach to the rationalization of tanning processes.

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List of symbol

a half length of pores [m]
b - half thickness of cured hide [m]
c - volume concentration of NaCl in cured hide [kg m^{-3}]
c_0 - volume concentration of NaCl in drum bath [kg m^{-3}]
D - effective diffusion coefficient of NaCl in cured hide [m^{2}s^{-1}]
Fo Fourier number – dimensionless time [1]
$m(\tau)$ mass of sodium chloride transferred from the hide into the bath during the time τ [kg]
$m(\infty)$ total mass of sodium chloride to be transferred from the hide into the bath before the system reaches equilibrium [kg]
S surface area of solid state [m^2]
V - volume of technological water [m^3]
V_s - volume of cured hide [m^3]
x - Coordinate [m]
α dimensionless soaking parameter [1]
ε porosity of solid state [1]
λ transport coefficient [s^{-1}]
τ - Time [s]

Other symbols are explained in the text directly.

References

[1] Blaha, A. and K. Kolomazník, "Mathematical model of soaking. Part I.", *JSLTC* **73**, pp. 136 – 140 (1989).

[2] Brien, O', D. J., "A Mathematical Model for Unsteady State Salt Diffusion from Brine-Cured Cattlehides". *JALCA* **78**, p. 286 (1983).

[3] Corning, D. R., "The Chemical Engineer in the Tannery", *JSLTC* **56**, pp. 95 – 102, (1972).

[4] Crank, J. and G. S. Park, *Diffusion in Polymers*, A.P., New York (1968), p.16.

[5] Eddy, V. et al. *Radical Environmentally Sustainable Tannery Operation by Resource Management*, GROWTH Project GRD1-2001-40469 RESTORM, Eddy, V. (Ed.), British Leather Center Northampton, October 2001, Northampton.

[6] Felix, M. and K. Bláha, *Mathematical Statistics Methods in Chemical Industry*, 1st Ed., SNTL, Prague (1962), p. 336.

[7] Komanowsky, M. W. K. Heiland, G. E. Senske, N. C. Aceto and J. G. Craig, "Continuous Automatic Beamhouse Processing II. Adaptation of Chemical Operations to the Requirements of the Process", *JALCA* **78**, p. 300 (1983).

[8] Manh, T. P., V. Vašek and K. Kolomazník, "Best practices scrap leather recycling". *In: II. workshop US Asia Environmental Partnership - Nike*, January 2003, Ho Chi Minh City, Vietnam

[9] Nerst, W., "Zur Kinetik der in Lösung befindlichen Körper: Theorie der Diffusion", *Z. Phys. Chem.* **2**, pp. 613-637 (1888).

[10] Perry, R. H., C. H. Chilton and S. D. Kirkpatrick (Eds.), "Chemical Engineer's Handbook", 5th Ed., McGraw – Hill, New York, London (1969), pp. 3-235.