Computer simulation and verification of deliming process mathematical model

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***Abstract*—**The paper deals with chemical deliming process that is one of operations of natural hides treatment. Nowadays, this process is characterized by great consumption of water, chemical agents and electrical energy needed for sufficient decrease of lime in processed hides. Therefore we search optimal technological procedure that will be advantageous from both economic and ecological aspects. We describe method that we used to determination of fixing power which is lime bound to collagen fibers of pelt. This data enabled us to verify mathematical model that we formulated for description of removing of lime from pelt during deliming in the bath system.

***Keywords*—**Mathematical model, deliming process, pelt, sorption coefficient determination, chelatometric titration.

I. Introduction

Deliming belongs to tannery operations of natural hides treatment. Deliming prepares pelts (hides prepared for deliming) for following tannery operations. The purposes of deliming can be sumarized as [1]:

- removing of lime (calcium hydroxide) from pelts,
- lowering the pH in the pelt suitable for biochemical reaction of protease (bating),
- reduction of swelling of pelt.

Lime is in the pelt partly bound to collagen fibers. Therefore deliming is realized in two steps. First the unbound lime is mechanically removed by pure water. In the second step the bound lime is removed by use of chemical agents (acids and acid salts).

In practice, these operations are characterized by great consumption of water, chemical agents and electrical energy needed for sufficient decrease of lime in processed hides. Therefore we search optimal technological procedure that will be advantageous from both economic and ecological aspects [2].

II. Mathematical model of deliming process

By reason of deliming liquid consumption lowering, deliming process is mostly realized by washing of pelts in the bath without inflow and outflow of deliming liquid.

By formulation of mathematical model of deliming we assumed that all lime will solute in deliming liquid and that pure water will be used as deliming liquid. This process can be described by one-dimensional second Fick's law [1], [3], [4]

$$\frac{D}{A+1}\cdot\frac{\partial^2 c(x,\tau)}{\partial x^2}=\frac{\partial c(x,\tau)}{\partial \tau}\quad,\ \tau>0,\ 0\le x\le b \tag{1}$$

Initial uniform distribution of lime in the pelt is given by equation (2)

$$c(x,\ 0)=c_p \tag{2}$$

Equation (3) gives an initial concentration of calcium ions in deliming liquid

$$c_0(0)=0 \tag{3}$$

Diffusion of calcium ions from pelt into the deliming liquid as symmetric problem can be described by condition (4)

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

Equation (5) assumes a perfectly mixing of liquid phase

$$c(b,t)=\varepsilon\cdot c_0(\tau) \tag{5}$$

Boundary balance condition (6) denotes the equality of the diffusion flux at the boundary between the solid and the liquid phases with the speed of accumulation of the diffusing element in the surrounding.

$$\frac{\partial c}{\partial x}(b,\tau)=-\ \frac{V_0}{D\cdot S}\ \cdot\ \frac{\mathrm{d}c_0}{\mathrm{d}\tau}(\tau) \tag{6}$$

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Fixing power of calcium ions in the pelt represented by sorption coefficient A in diffusion equation (1) can be determined from Langmuir sorption isotherm (7)

$$c_A = \frac{Ac}{Bc+1} \tag{7}$$

For very small concentrations of calcium ions can be written

$$c_A = K \cdot c \tag{8}$$

where $K \approx A$.

For simplification of mathematical solving of above-mentioned model we introduced dimensionless parameters.

Parameter C is dimensionless concentration of calcium ions in the pelt (9)

$$C = \frac{c}{c_p} \tag{9}$$

C_0 is dimensionless concentration of calcium ions in the deliming liquid (10)

$$C_0 = \frac{c_0}{c_p} \tag{10}$$

Symbol X is a dimensionless space coordinate (11)

$$X = \frac{x}{b} \tag{11}$$

F_o is dimensionless time of process (Fourier criterion) (12)

$$F_0 = \frac{D \cdot t}{b^2 \cdot (1+A)} \tag{12}$$

Symbol Na is dimensionless volume of deliming liquid (13)

$$Na = \frac{V_0}{V} \tag{13}$$

By means of Laplace transformation we obtained analytic solution describing dimensionless concentration field $C(X, F_o)$ in the pelt [5]:

$$C(X,F_o) = \frac{\varepsilon(1+A)}{\varepsilon(1+A)+Na} - 2Na \cdot \sum_{n=1}^{\infty} \frac{\cos(q_n X)\exp(-q_n{}^2 F_0)}{\varepsilon(1+A)\cos(q_n) - \frac{\varepsilon(1+A)}{q_n}\sin(q_n) - Na \cdot q_n \sin(q_n)} \tag{14}$$

where q_n are computed according to equation (15)

$$-\frac{Na \cdot q}{\varepsilon \cdot (1+A)} = \tan(q) \tag{15}$$

III. EXPERIMENTAL DETERMINATION OF DELIMING PROCESS COURSE

As we mentioned in previous section, the fixing power of calcium ions on collagen fibers of pelt belongs to main parameters which influence deliming process course.

Total quantity of calcium ions in deliming system can be computed as a sum of quantity of the calcium ions both free and fixed in the pelt, and also quantity of calcium ions, which moved into the bath [1]

$$\boxed{\underbrace{c_S \cdot V}_{\text{total weight of calcium ions in the system}} = \underbrace{c_A \cdot V}_{\text{weight of calcium ions bound to the pelt}} + \underbrace{c \cdot V}_{\text{weight of unbound calcium ions in the pelt}} + \underbrace{c_0 \cdot V_0}_{\text{weight of calcium ions in the deliming liquid}}} \tag{16}$$

By substitution of the equation (8) into the balance equation (16) we obtained equation suitable for estimation of the coefficient K or A:

$$\frac{c_S}{c_0} = \varepsilon \ (K+1) + Na \tag{17}$$

Laboratory testing of deliming process course consisted in determination of bound component concentration c_A on unbound component concentration c in the pelt. We used linear equation (17) for determination of sorption coefficient A. Tested cattle pelts were supply by Tarex Ltd, Otrokovice, Czech Republic.

For determination of dependence $1/c_0$ on Na, we put cut-up pelt samples of various weight into the wash bottles, which had identical volumes of deliming liquid, so that soak numbers were between 1 and 10 (Fig. 1, Fig. 2). Then we kept them in the nitrogen atmosphere till equilibrium state achievement.

Fig.1. Pelt samples prepared for laboratory testing

Fig.2. Laboratory apparatus for determination of deliming process course

We determined Concentration of calcium ions in the deliming liquid (c_0) by chelatometric titration. The method principle is based on addition of Complexone III of defined concentration into deliming liquid samples. Murexide was used as an indicator. Chemical reaction of total calcium ions with Complexone III caused color change of tested samples (Fig. 3) [6].

Fig.3. Colour change of tested samples by chelatometric titration – sample before titration (on the left) and sample after titration (on the right)

The Fig. 4 depicts determined sorption isotherm of calcium oxide by washing computed for tested samples of pelt. Value of the sorption coefficient calculated according equation (11) was $K = 3.956$. Supposed porosity of the pelt sample was $\varepsilon = 0.5$ [1], [5].

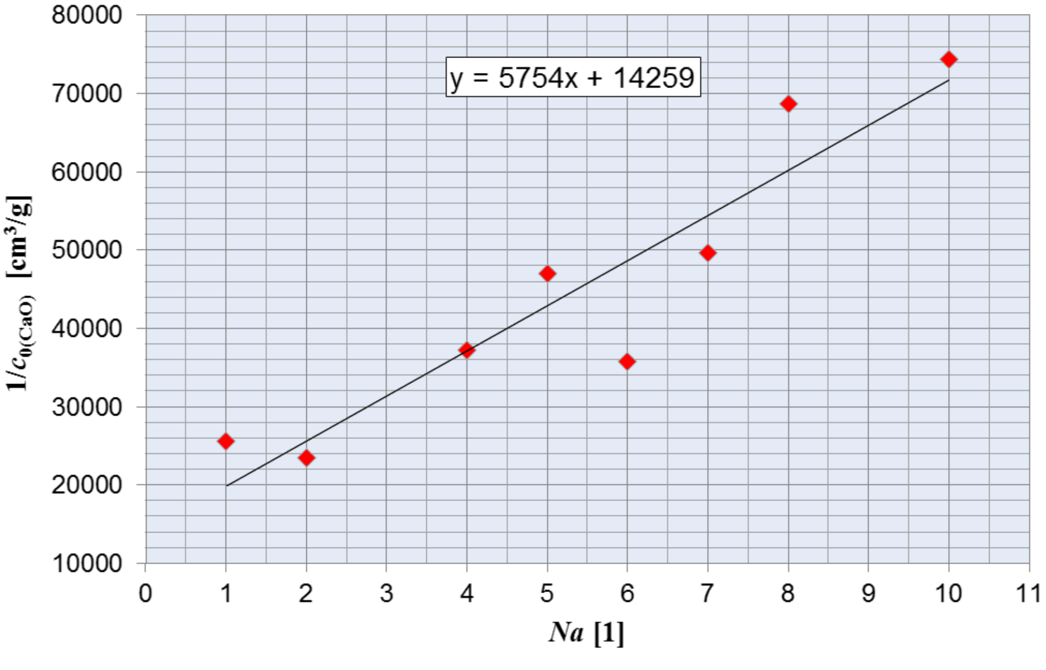
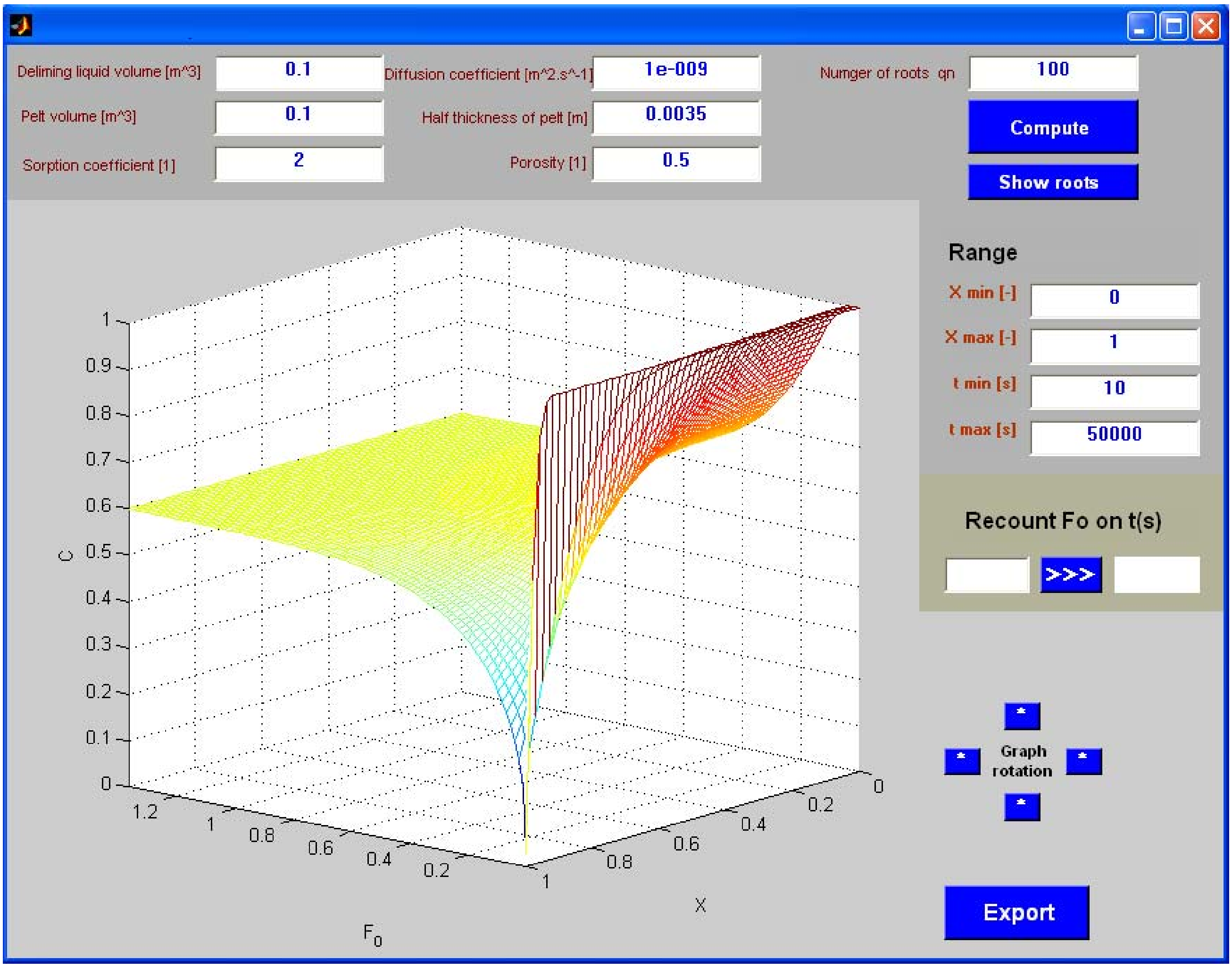


Fig. 4 Sorption isotherm of calcium oxide by washing before deliming (washing time: 48 hours)

IV. SIMULATION OF DELIMING PROCESS

For computer simulation of deliming process course we used special software application programmed in Matlab user environment (Fig. 5) [3]



Deliming liquid volume [m^3] 0.1
Diffusion coefficient [m^2.s^-1] 1e-009
Numger of roots qn 100
Pelt volume [m^3] 0.1
Half thickness of pelt [m] 0.0035
Sorption coefficient [1] 2
Porosity [1] 0.5

Range
X min [-] 0
X max [-] 1
t min [s] 10
t max [s] 50000

Fig. 5 User interface of software application for modeling of deliming process

We used the experimentally determined value of fixing power for computing of concentration field of the washed lime in the pelt (10). The other needed parameters as are diffusion coefficient and porosity we took over from previous testing [1], [5] of deliming process course:

Volume of deliming liquid V: 1 m^3
Volume of pelt in bath V_0: 13 m^3
Thickness of pelt $2b$: 3.5 mm
Effective diffusion coefficient D: $1\cdot10^{-9}$ m$^2\cdot$s^{-1}
Porosity of pelt material ε: 0.5
Fixing power A: 3.56

Fig. 6 and Fig 7 show computed temperature fields in tested pelt. The results proved that pure water as deliming liquid has washed only about 30 % of the total mass of lime from tested samples. It is clear, that remaining lime have to be removed by some chemical deliming agent.

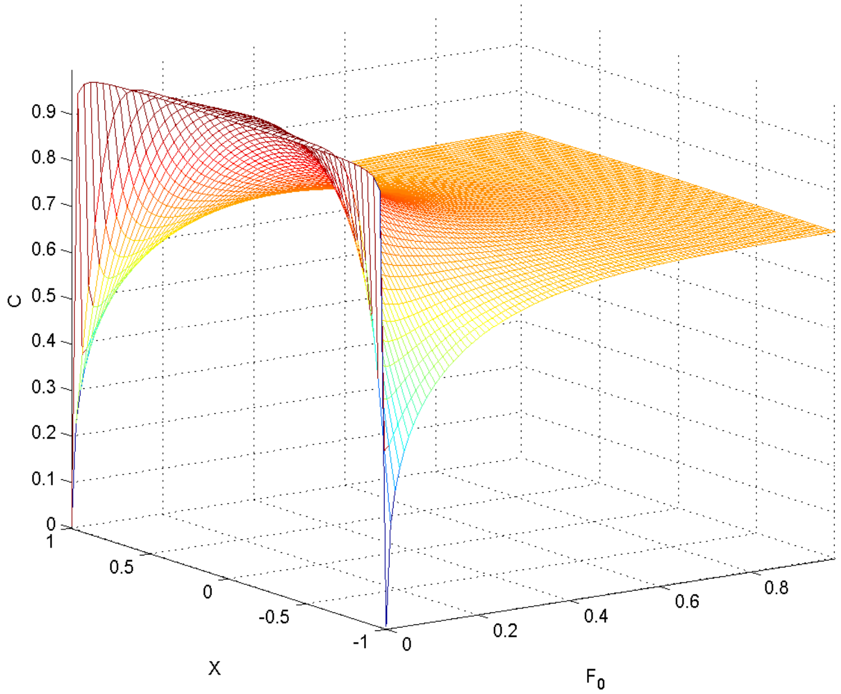


Fig. 6 Computed dimensionless concentration field in the pelt

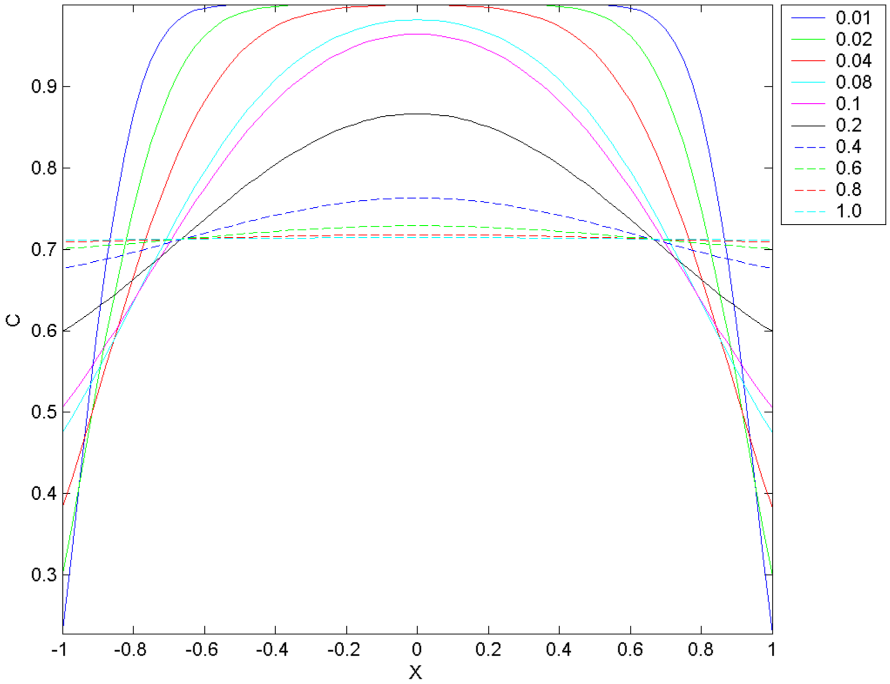


Fig. 7 Computed concentration fields in the pelt in specific dimensionless times of deliming

V. DELIMING PROCESS OPTIMIZATION

According to solution of mathematic model of deliming washing process (14) , it is possible to find the optimum of deliming liquid of process to be successful course of the process respectively, and that all from the corresponding the cost function [8], [10], [11].

To determination of the cost function for the material bath washing we assumed that we are able to eliminate component from the material by the deliming liquid and that the main processes costs N_C of considered process are given by the sum of the consumed electric energy to the drive of machinery costs N_E and the consumed deliming liquid costs N_V

$$N_C = N_V + N_E \tag{18}$$

whereas the consumed electric energy costs are given by the product of the electric power unit price K_E, the time t and the electromotor input P to the drive of machinery

$$N_E = K_E \cdot P \cdot t \tag{19}$$

The costs of the deliming liquid requirements N_V are given by the product of unit price of deliming liquid K_V and the deliming liquid volume V_0

$$N_V = K_V \cdot V_0 \tag{20}$$

We supposed as well that the increasing deliming liquid requirements cause the decreasing of deliming liquid pollution during the washing whereby the effectiveness of washing process increases. Thereby the time interval, necessary to the drive of machinery is shorter, hence the electric energy costs are decreasing because these are linearly increasing with dependence on time. This implies that the sum of the deliming liquid requirements costs and the electric energy in dependence on the deliming liquid requirements keeps a minimum.

If we want to determine the total costs in dependence on the total dimensionless deliming liquid requirements then first it is necessary to determine the dependence of the washing degree y, which determines the efficiency of the washing process in dependence on the dimensionless time F_o and that for the corresponding soak number Na. Dependence of the washing degree y, on the dimensionless time F_o is given by equation (21) [5]

$$y = \frac{C_0 Na}{1+A} = \\ = \frac{Na}{\varepsilon\left(1+A\right)+Na} - 2\frac{Na^2}{\varepsilon\left(1+A\right)}\sum_{n=1}^{\infty}\frac{\exp\left(-F_o\ q_n^{2}\right)}{\varepsilon\left(1+A\right)+\dfrac{q_n^{2}Na^2}{\varepsilon\left(1+A\right)}+Na} \tag{21}$$

In the Fig. 4 is depicted dependence of the washing degree on the time. The time is computed from Fourier number according to equation (12)

Determination of time to reaching demanded washing degree of given soak number enable to compute cost function according to equation (22)

$$N_C = K_V \cdot Na \cdot V + \frac{K_E \cdot P \cdot F_o \cdot b^2 \cdot (1+A)}{D} \tag{22}$$

Minimum of the function (23) determines optimal soaking number for the process, which is ratio of volume of deliming liquid to volume of pelt (13).

VI. DETERMINATION OF DELIMING PROCESS COST FUNCTION

For determination of optimal soaking number, we computed first dependence of the washing degree y, on the dimensionless time F_o (Fig. 7). Conditions of the process :

Volume of deliming liquid V:	1 m^3
Volume of pelt in bath V_0:	13 m^3
Thickness of pelt $2b$:	3.5 mm
Effective diffusion coefficient D:	$1 \cdot 10^{-9}\ m^2 \cdot s^{-1}$
Porosity of pelt material ε:	0.5
Fixing power A:	3.56
Input of electromotor to the drive of machinery P:	1kWh
Electric power unit price K_E:	$0.25€ \cdot kW^{-1} \cdot h^{-1}$
Unit price of washing liquid K_V:	$2.5\ € \cdot m^{-3}$
Required washing degree y_0:	0.35

The optimal soaking numbers we computed for deliming degrees 0.,3, 0.4, 0.5, 0.6. The computed data we show in Fig. 9 – Fig. 13. As you can see, the optimal soaking number increase with increasing required washing degree. By washing degree 0.3 the optimal soaking number is 1.9. By washing degree 0.4 the optimal soaking number is about 2.85.. By washing degree 0.5 the optimal soaking number is about 4.2 and by washing degree 0.6 the optimal soaking number is about 5.9.

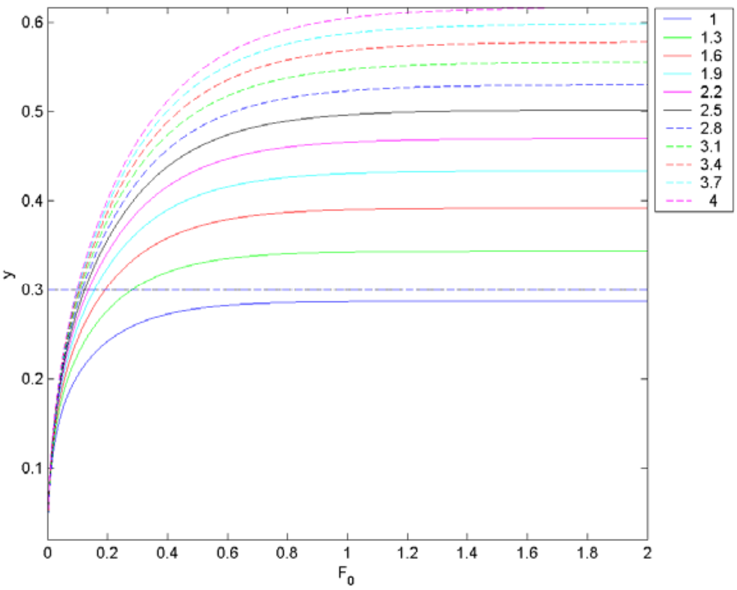


Fig. 8 Dependence of the washing degree *y* on the dimensionless time F_o

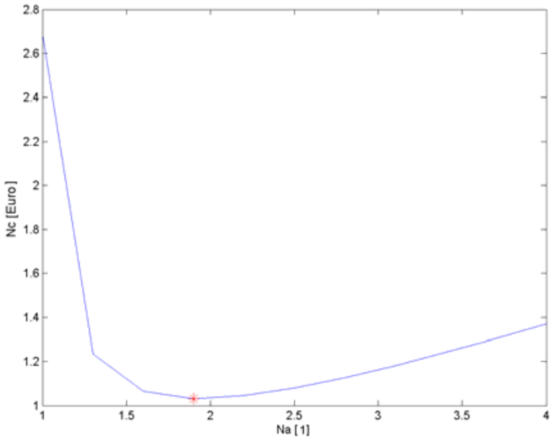


Fig. 9 Computed cost function for washing degree 0.3

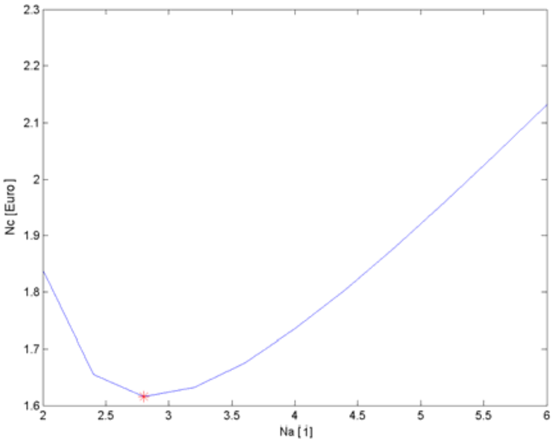


Fig. 10 Computed cost function for washing degree 0.4

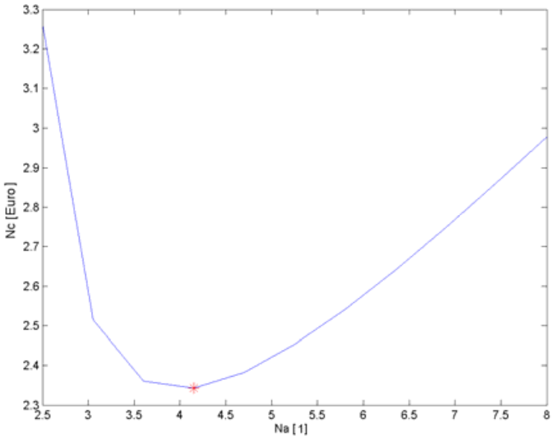


Fig. 11 Computed cost function for washing degree 0.5

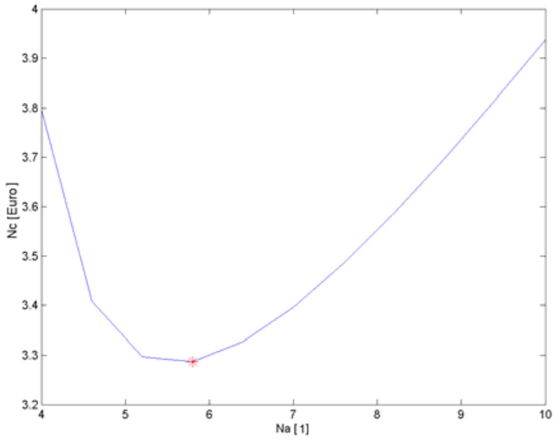


Fig. 12 Computed cost function for washing degree 0.6

VII. CONCLUSION

In the paper we presented results which we obtained by verification of mathematical model of deliming process by use of pure water as deliming liquid. By experimental testing of deliming process course of cattle pelts we have determined fixing power of lime in the pelt about 3.97. By mathematical modeling of the process course for this value of fixing power, we have found out that pure water as deliming liquid has washed only about 30 % of total mass of lime from the tested samples. Computed cost function enables to find the optimum of deliming liquid.

The obtained results along with other testing of deliming process course will lead to finding an optimal technological procedure that will be advantageous from both economic and ecological aspects. is given by equation.

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VIII. LIST OF SYMBOLS

Symbol	**Meaning**	**Unit**
V	volume of pelt	m^3
V_0	volume of washing liquid	m^3
t	time	s
c	volume concentration of calcium ions in pelt	$kg \cdot m^{-3}$
c_0	volume concentration of calcium ions in bath	$kg \cdot m^{-3}$
c_p	initial concentration of calcium ions in pelt	$kg \cdot m^{-3}$
c_A	volume concentration of calcium ions bound into pelt	$kg \cdot m^{-3}$
D	effective diffusion coefficient	$m^2 \cdot s^{-1}$
x	position coordinate	m
b	half thickness of pelt	m
ε	porosity of pelt	1
Na	soaking number	1
q_n	n^{-th} root of a certain transcendent equation	1
A	sorption coefficient (fixing power)	1
B	sorption coefficient	$m^3 \cdot kg^{-1}$
S	area of pelt	m^2
F_o	Fourier number	1
C	dimensionless volume concentration of calcium ions in pelt	1
C_0	dimensionless volume concentration o fcalcium ions in bath	1
X	dimensionless space coordinate	1
y	washing degree	1
y_0	required washing degree	1
P	input of electromotor to the drive of machinery	kWh
K_E	electric power unit price	$€ \cdot kW^{-1} \cdot h^{-1}$
K_V	unit price of washing liquid	$€ \cdot m^{-3}$
N_E	electric energy to the drive of machinery costs	€
N_V	deliming liquid costs	€
N_C	the main processes costs	€

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