Modeling of Raw Hide Soaking

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Abstract: Raw hide, being an expensive starting material for manufacturing natural leathers, arrives in tanneries in a preserved state. In most cases, sodium chloride is used as preservation medium. In a whole number of operations through which raw hide is transformed into leather, raw hide desalting is a very important operation in view of final quality. The procedure incorrectly executed may cause considerable damage to edge parts of raw hide, effecting considerable economic losses in final area yield of leather substance. Another important factor playing a great role is environmental protection. The tanning industry consumes considerable amounts of power, chemicals and technological water, thus producing a great quantity of waste liquids. From this viewpoint, a specific optimum of processing procedures should also be sought. Hence, the presented paper deals with desalting of raw hides, meaning soaking operations when viewed from the position of tanner.

Key-Words: Optimization, Ecology, Economic system, Waste Treatment, Environmental Engineering

1 Introduction

The process of raw hide desalting is associated with dissolving kinetics of a solid salt adhering to the surface and inside hairy spaces of hide on the one hand, and on transport of sodium chloride ions from the inner volume of hide mass. There are thus two desalting process mechanisms – kinetic, related to dissolving solid surface salt, and diffusion, related to transport mechanisms, i.e. to internal diffusion (e.g. Kirk-Othmer, 1992). This contribution mainly deals with the kinetic mechanism taking place in the first stage of desalting process, i.e. through dissolving of solid salt (Dean, 1992) and the optimization of the process from the operational point of view.

2 Kinetic mechanism

Desalting is performed in rotating cylindrical reactor - tanning drum in which salted hides and water are loaded (Rangarajan, *et al*., 2003; Venkatachalam, *et al*., 1982). Drum rotation is produced by means of electric motor.

Main general operating costs N are given by sum of costs of power N_E for rotation by electric motor and of consumed technological water N_W (desalting solution).

$$N = N_E + N_W = P\,K_E\,\tau + V\,K_v \qquad (1)$$

The complete list of symbols is described at the end of the article. Time τ in equation (1) naturally depends on the volume of technological water. In order to derive this dependency, it is assumed that rate of surface salt dissolution is proportionate to difference between concentration of saturated solution and immediate concentration of salt in technological water. The relation can be expressed by a differential equation:

$$\frac{da}{d\tau} = k\left(a_n - a\right) \qquad (2)$$

The desalting degree x is defined as

$$x = \frac{a m_v}{a_p m_s} = \frac{a \rho_v V}{a_p \rho_s V_s} \approx \frac{a}{a_p} \cdot N_a \qquad (3)$$

where $N_a = \dfrac{V}{V_s}$ (soaking number). $\qquad$ (3a)

The function $a(\tau)$ in (2) can be derive from (3) by:

$$a = \frac{x a_p}{N_a} \qquad (4)$$

and after some substitution and derivation a similar equation is obtained in the form:

$$\frac{dx}{d\tau} = k\left(K - x\right) \qquad (5)$$

where the parameter K is given by

$$K = \frac{a_n N_a}{a_p} \qquad (5a)$$

Integration of (5) gives

$$\tau = -\frac{1}{k}\ln\left(1-\frac{x}{k}\right) \qquad (6)$$

and after the substitution for τ from equation (6) into (1) the final relation for operating costs is given by:

$$N = K_v V - \frac{1}{k}\ln\left(1-\frac{x}{K}\right) \qquad (7)$$

This function is the proper cost function for an optimizing process which results in optimal industrial operating conditions.

3 Experimental results

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

$$\ln\left(\frac{a_n}{a_n-a}\right) = k\tau \qquad (8)$$

Plotting natural logarithm $a_n\,(a_n-a)^{-1}$ as a function of time, it is obtained a straight line whose gradient gives the value of rate constant k of dissolving salt.

$$\frac{\partial c(x,\tau)}{\partial \tau} = D\frac{\partial^2 c}{\partial x^2} \qquad (9)$$

During dissolving of salt, dissociation into Na^+ cations and Cl^- anions takes place, making possible the conduction of current.
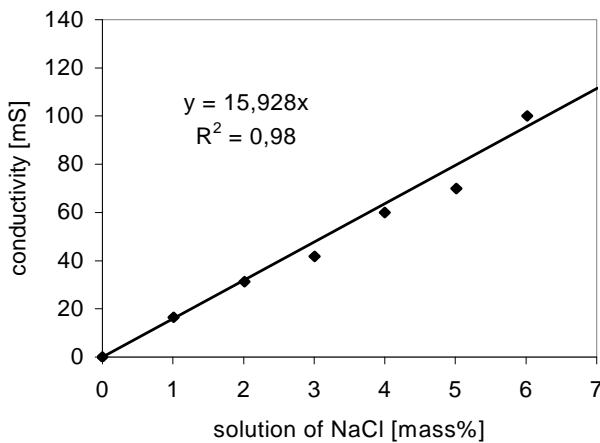

Fig. 1. Calibration curve.

Conductivity of the solution of produced electrolyte is dependent on ionic concentration, charge magnitude of individual ions, on solution temperature and mobility of

Table 1 Dependence of electric conductivity on concentration of sodium chloride in aqueous solution

NaCl [g]	solution [g]	mass% solution	conductivity [mS]
0	100,0000	0	0,00395
1,0069	100,0599	1,006	16,5
2,0109	100,0426	2,010	31,2
3,0099	100,1005	3,007	41,8
4,0013	100,0530	3,999	60,0
5,0120	100,0003	5,012	70,0
6,0238	100,0878	6,019	100,0
7,0087	100,0008	7,009	120,0

ions in electric field. For conductivity measurements the conductometer OK 102/1 with bell electrode Radelkis OK-9023 was employed.

Then the calibration curve, i.e. dependence of conductivity on sodium chloride concentration was constructed. Seven samples of various concentrations of salt (NaCl) were prepared and their conductivities measured. Results of measuring are shown in Table 1 and depicted in Fig. 1.

The dissolving 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 120ml volume tempered at $20^\circ C$ was suddenly added approximately 4.4g salt. Conductivity measurements were read at 5s intervals. A table was drawn up from obtained values and concentration determined by means of calibration curve. Experiment results can be seen in Table 2 and Fig. 2. Fig. 3 shows the dependence of natural logarithm of difference in concentration of salt on time (τ). The adventitious curve is serving to evaluate of dissolving rate constant k according to equation (8).
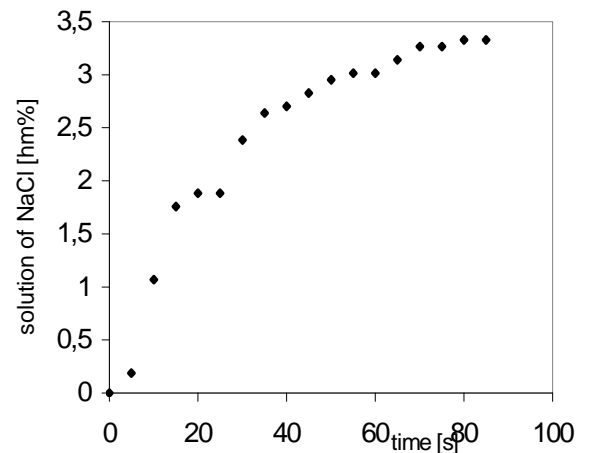

Fig. 2. Dependence of changes in concentration of salt solution on time

4,5
4
y = 0,0465x
R² = 0,9443
3,5
3
2,5
2
1,5
1
0,5
0

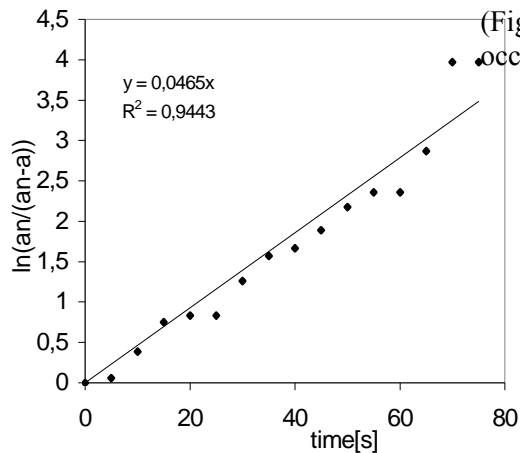ln(an/(an-a))

0   20   40   60   80
time[s]

Fig. 3. 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}.

Table 2 Kinetics of surface salt dissolving

time [s]	conductivity [mS]	conc.a [mass%]	$\ln(a_n/(a_n-a))$
0	0,0023	0	0
5	3	0,1883	0,0583
10	17	1,0673	0,3868
15	28	1,7579	0,7514
20	30	1,8835	0,8348
25	30	1,8835	0,8348
30	38	2,3857	1,2622
35	42	2,6369	1,5724
40	43	2,6996	1,6675
45	45	2,8252	1,8908
50	47	2,9508	2,1785
55	48	3,0136	2,3609
60	48	3,0136	2,3609
65	50	3,1391	2,8714
70	52	3,2647	3,97
75	52	3,2647	3,97
80	53	3,3275	
85	53	3,3275	

3. SIMULATION CALCULATIONS

In practical desalting of raw hides three cases may occur. The first is very similar to dissolving pure salt. This situation seldom appears because salt is considerably polluted with low-molecular ingredients such as soluble amino acids, fats, dirty particles and the like (Eaton, *et al.*, 1995). It is shown in Fig. 5 for dissolving rate constant equalling 160 h^{-1}. The second case involves weakly polluted salt particles with a dissolving rate constant of 16 h^{-1} (Fig. 6), and finally the third case involves strongly polluted salt particles, where the dissolving rate constant has a value of 1,6 h^{-1}

Common starting parameters applied in all cases were as follows:

Economic parameters: $K_E = 0,12$ EUR kWh^{-1}
$K_v = 1,3$ EUR m^{-3}

Technological parameters: $x = 0,999$
$V_s = 10$ m^3
$a_n/a_p = 1$
$P = 20$ kW

The final procedure of the desalting operation process consists of following steps. The flow chart of this procedure is depicted in Fig. 4:

Data input **1.**

Calculation of start. optim. data **2.**

Dosage of water **3.**

Optimisation calculation **4.**

Identification $\tau > \tau_{opt}$ **5.**
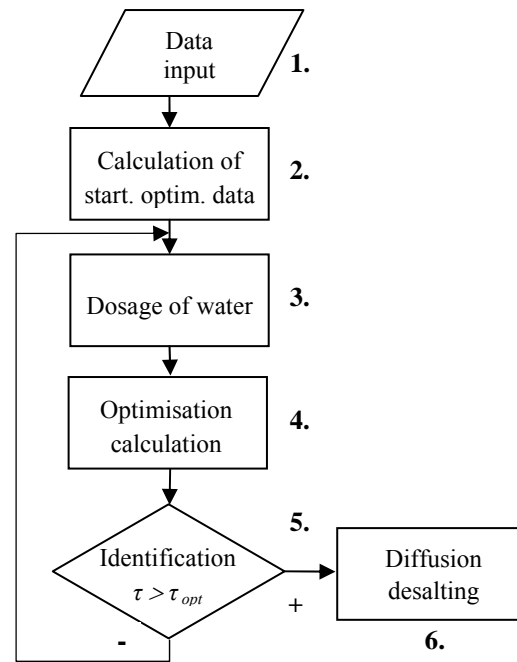
Diffusion desalting **6.**

+

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Fig. 4. Flow chart of a controlled raw hide desalting operation

1. Input of technical and economical data – common initial parameters and conditions: K_E, K_v, P, x, V_s, a_n/a_p and estimated value of rate constant of dissolving k.
2. Starting calculation of optimum volume of desalting solution V_{opt} and optimum desalting time τ_{opt}.
3. The volume of 50% calculated amount of desalting solution V_{opt} is dosed into the plant and then the solution conductivity is measured. Then, the actual value of rate constant of dissolving k is calculated.
4. Calculation of optimum volume of desalting solution V_{opt} and optimum desalting time τ_{opt} is repeatedly performed for actual value of rate constant of dissolving k. The dosage of desalting solution is always 50% of calculated volume.

The process of surface salt desalting finishes when

desalting time exceeds calculated optimum time τ_{opt}.

6. After finishing surface salt desalting, part of solution is removed and the rest diluted with further water. The diffusion desalting process begins.

Optimal consumption of desalting solution for rate constant k=160 h^{-1} is V_{opt}=10,001 m^3, optimal desalting time τ_{opt} = 0.04 h = 2,54 min, optimal total costs N$_{opt}$ = 13,10 EUR (see Fig. 5).

Fig. 5. Dependence of total costs on consumption of desalting solution for k=160 h^{-1}

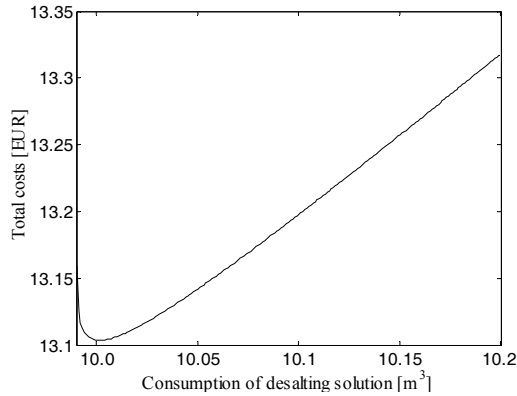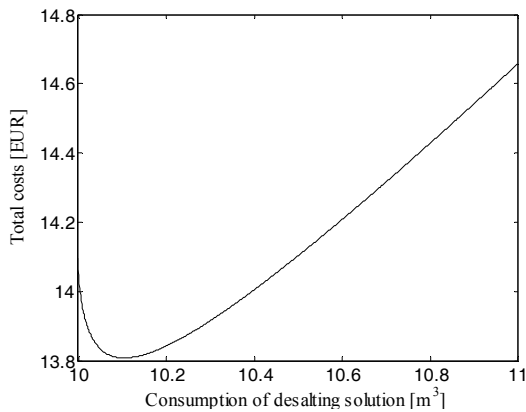Fig. 6. Dependence of total costs on consumption of desalting solution for k=16 h^{-1}
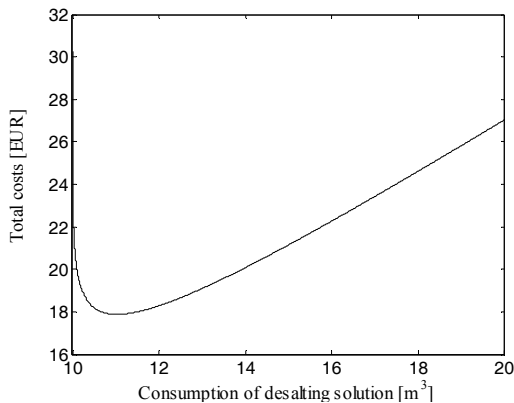

Fig. 7. Dependence of total costs on consumption of desalting solution for k=1,6 h^{-1}

Optimal consumption of desalting solution for rate constant k=16 h^{-1} is V_{opt}= 10,10 m^3, optimal desalting time τ_{opt} = 0.28 h = 16,81 min, optimal total costs N = 13,81 EUR (see Fig. 6).

Optimal consumption of desalting solution for rate constant k=1,6 h^{-1} is V_{opt}= 11,03 m^3, optimal desalting time τ_{opt} = 1,47 h = 88,40 min, optimal total costs N = 17,88 EUR (see Fig. 7).

4. Diffusion mechanism

After removal of surface solid salts, the inner volume of raw hide contains a virtually saturated solution of sodium chloride. Na$^+$ and Cl$^-$ ions get through inner diffusion to the surface of raw hide and from there into diluted surrounding solution. The system in question is then one of distributed parameters where the state quantity – sodium chloride concentration – is a function not merely of time but also of position, and a dynamic model of the system is given by a partial differential equation or in the simplest case by Fick's second law.

The situation is all the more complex as thickness of raw hide alters from a low value – flank - to a high value in the butt, whereby one-dimensional diffusion changes into two-dimensional.
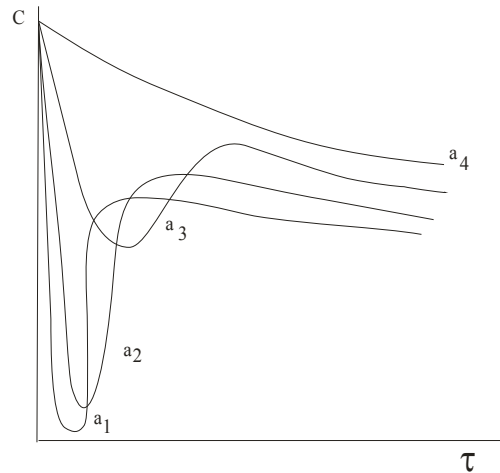

Fig. 8. Dependence of concentration of salt on time for different thickness of hide (from low value - a_1 to a high value - a_4)

This state of affairs is complicated by the fact that concentration decreases and again grows up during desalting, particularly near the surface and in places of low thickness thus causing considerably varying osmotic pressures in a very short time interval. Hence, damage of border parts of raw hide bends can appear. This fact is linked with substantial economic losses and with an environmental load by produced wastes (Rangel-Serrano, et al., 2003). Demonstration of the dependence of concentration of salt on time for

different thickness of hide (from low value -a_1 to a high value - a_4) is depicted in Fig. 8.

Obviously, the preceding procedure cannot be employed even if a corresponding solution to the model of a dynamic system with distributed parameters was found (Kanagaraj, *et al.*, 2000). For this reason and from practical experience the solution was proposed in the process where desalting the inner volume of hide takes place gradually by washing in a solution of salt at a starting concentration equal to approximately half the starting concentration of salt in solid phase (Hankey, *et al.*, 2001; Marmer, 2001). This acquisition causes that the concentration of salt continuously decreases during desalting and consequently avert damage of thin part of raw hide.

5. Conclusions

The presented paper deals with desalting of raw hides, meaning soaking operations - mainly with the kinetic mechanism taking place in the first stage of desalting process. In a whole number of operations through which raw hide is transformed into leather, raw hide desalting 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.

The developed results demonstrate that the specific optimum volume of technological water (desalting solution) and the total costs for desalting process can be found. Further authors recommendations suggest to continue in this way and to establish optimal process for diffusion desalting. It may optimize operating costs as well as avoid economic losses for incorrectly performed procedure and reduce quantity of waste liquids.

List of symbol:
P - electric motor input   [kW]
K_E - unit price of power   [EUR/kWh]
V - volume of technological water [m^3]
K_v - unit price of technological water   [EUR/m^3]
τ - 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 desalting process ($\tau = 0$) [l]
N_a - soaking number [1]
k - dissolving rate constant of salt   [h^{-1}]
m_v - mass of technological water [kg]
m_s - mass of raw hide   [kg]
ρ_v - density of technological solution [kg m^{-3}]
ρ_s - density of raw hide   [kg m^{-3}]
V_s - volume of raw hide   [m^3]
x - required leather desalting degree [l]

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