Modeling of Bound Component White Hide Deliming

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Abstract: - Many technological processes are characterized by large consumption of water, electrical energy and auxiliary chemicals. No even the tanning industry is the exception.
The contemporary worldwide trend is an application of the cleaner production principles, which means to take the line of savings and minimization of waste production. It is necessary to deal with the optimization of processes.Within the optimization of the white hide deliming operation, both plain washing with pure water and chemical processing are concerned. The main goal is to give the answer to when it is suitable to interrupt the washing with pure water (non-chemical deliming) and replace it by washing with a deliming agent water solution (chemical deliming). Our paper, with the use of a mathematical-physical process model, gives the answer to the above mentioned question. The effective diffusion coefficients are presented. The above mentioned parameters, economical and technological serve as input data for a computer program and the proposal of automatics control algorithm.

Key-Words: - Optimization, Mathematic modeling, Tannery process, Deliming.

1 Introduction

Unhaired hide reacts strongly alkali due to the content of sodium sulphide and lime as a result of employing these chemicals in the unhairing process. The alkalinity of raw hide has to be decreased because the following processes proceed in acid conditions. The changes from alkalinity to acidity proceed gradually to prevent the fine fibrous hide structure from being damaged. Sodium sulphide and partly calcium hydroxide are removed by washing with pure water. The rest of the lime is eliminated with the use of auxiliary deliming chemicals due to its strong bond with collagen protein. Deliming agents break bounds between lime and collagen protein, resulting in neutral salts. There exist many acid reacting chemicals that are able to perform the chemical deliming process. Nowadays, environmentally friendly criteria should he applied to choose from those chemicals. Unfortunately, most of the environmentally friendly deliming agents are more expensive than those used till now (ammonium sulphate for example). For this reason the optimization of the deliming process becomes more topical.
The optimization of the white hide deliming operation concerns both plain washing with pure water and a chemical processing. The main goal is to give the answer to when it is suitable to interrupt the washing with pure water (non-chemical deliming) and replace it by washing with deliming agent water solution – chemical deliming.

2. Theory

The exact mathematical model of the processes, especially of the chemical deliming, is too complicated; therefore from the practical point of view we introduce useful criteria and necessary simplifications. The degree of the deliming operation (y) is defined as a ratio of removed lime mass (m) to the total (initial) lime mass in white hide (ms):

$$y = \frac{m}{m_S} = \frac{C_O V_O}{C_S V} = \frac{C_O}{C_S} Na \tag{1}$$

where we introduce an important technological parameter $Na = Vo/V$ as a dimensionless consumption of water or water solution of deliming agents. Another very important parameter is Fourier's number (dimensionless time) *(Fo)* defined by the following equation where:

$$Fo = \frac{k\tau}{b^2} \quad (2)$$

$$k = \frac{D}{1+K} \quad (3)$$

When we accept that the practical equilibrious process is reached for Fo~1, the operation time thus can be easily estimated from. Parameter k in the equation of (3) is a modified adsorption coefficient which can be estimated from the adsorption isotherm t, e, and the dependence of adsorbed lime concentration (C_A) on hide and on the free solution lime concentration (C) in the equilibrium conditions. Langmuir's isotherm is commonly used:

$$C_A = \frac{AC}{1+BC} \quad (4)$$

And for K: $$K = \frac{dC_A}{dC} = \frac{A}{(1+BC)^2} \quad (5)$$

K equationuals zero in the case of chemical deliming, i.e. $k=D$, equation. (3).

Main operating costs (N_{iN}, N_{iCH}) are given by the sum of costs of electric power for rotation by electric motors and the cost of consumed washing water (non-chemical deliming) or water solution of a deliming agent (chemical deliming) for an i – step operation.

$$N_{iN} = P\tau_{iN} K_E + K_V V_{oi} \quad (6)$$

$$N_{iCH} = P\tau_{iCH} K_E + K_{CH} V_{oi} \quad (7)$$

$$N_N = \sum_{i=1}^{n} N_{iN} \quad (8)$$

$$N_{CH} = \sum_{i=1}^{n} N_{iCH} \quad (9)$$

By combination of the equations we received the operation times of deliming process:

$$\tau_{iN} = \frac{b^2\left[\left(1+Bc_i\right)^2 + A\right]}{D\left(1+Bc_i\right)^2} \quad (10)$$

$$\tau_{CH} = \frac{b^2}{D} \quad (11)$$

2.1 Deliming degree calculation

2.1.1 Non-chemical deliming

Step 1; balance equation:

$$C_S V = C_{o1} V_{o1} + C_1 V_1 + V c_{A1} \quad (12)$$

By employing of the (4) we get:

$$c_S V = c_{o1} V_{o1} + V\varepsilon c_{o1} + \frac{A\varepsilon c_{o1} V}{1+B\varepsilon c_{o1}} \quad (13)$$

By solving of the (13) we receive

$$C_{01} = \frac{\varepsilon C_S B - Na_i - \varepsilon A - \varepsilon + \sqrt{\left(\varepsilon C_S B - Na_i - \varepsilon A - \varepsilon\right)^2 + 4C_S P}}{2P} \quad (14)$$

Total non-chemical deliming degree y_N is the sum of degrees in an i – step operation:

$$y_N = \sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{Co_i V_{oi}}{V \cdot C_S} = \sum_{i=1}^{n} \frac{Na_i Co_i}{C_S} = \frac{1}{C_S} \sum_{i=1}^{n} Co_i Na_i \quad (15)$$

$Na_i = 1$, for $i = 1,2 \ldots n$

2.1.2 Chemical deliming

Balance equationuations are the same, but A equationuals zero, resulting in that c_A is zero too.

$$c_s V = c_{o1} V_{o1} + \varepsilon c_{o1} V \quad (16)$$

And

$$\varepsilon C_{oi} V = C_{oi+1} V_{oi} + \varepsilon C_{oi+1} V \quad (17)$$

That means:

$$y_{CH} = \sum_{i=1}^{n} y_{CHi} = \sum_{i=1}^{\infty} \frac{Na_i Co_i}{c_p} = 1 - \left(\frac{\varepsilon}{\varepsilon + Na_i}\right)^n \quad (18)$$

because y_i are members of geometric sequationuence with quotient = $\varepsilon/(\varepsilon + Na_i)$,

$Na_i = Na_1 = Na_2 = Na_3 \ldots\ldots Na_n$ are in the above equations and $c_i = \varepsilon Co_i$ are used.

Using the equations (18) we receive the main operating costs of both non-chemical and chemical processes as a function of deliming degree and the sum of steps of the operations (n). The intersection of the above mentioned functions gives the interruption of the non-chemical deliming and its replacing by the chemical operation.

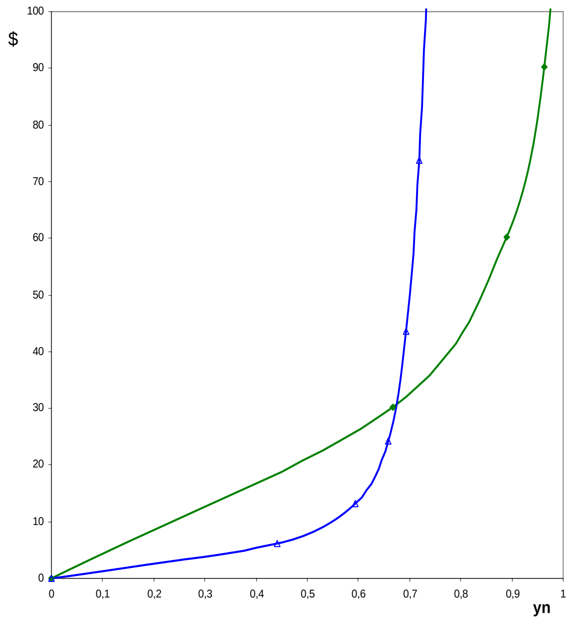

Figure 1: Cost curves

They are: Sorption coefficient *A* (fixing power of lime on a collagen surface) = 100
- Sorption coefficient $B = 57 m^3 kg^{-1}$
- Initial conc.of lime in hide $C_p = 5{,}1\ kg.m^{-3} \sim 0{,}5\%$
- Hide thickness $2b$ = 7mm
- Hide porosity $\varepsilon = 0{,}5$
- Soaking number $Na = 1$
- Effective diffusion coefficient of salt (calcium sulphate) $D = 10^{-10} m^2 s^{-1}$
- Unit price of technological water $K_V = 1$ USD m^{-3}
- Unit price of chemical deliming $K_E = 30$ USD m^{-3}
- Input power of drum electric motor $P = 15$ kW

The practically zero effectiveness of the non-chemical deliming results from the small initial concentration of lime in hide, which is approximately 0,5%; that means the process is found in an almost linear part of an adsorption isotherm, where the fixing power of lime on collagen surface is very strong. The initiation is quite different in the Figure2.
All the parameters are the same, only the initial concentration of lime in hide is four times higher (2%) than in the previous case. The lower starting curve represents non-chemical deliming. When it is sufficient to remove only 30% of lime, then only non-chemical deliming can be performed; if more than 40%, it is necessary to use chemical deliming as we can see in the Figure 1 (upper curve).

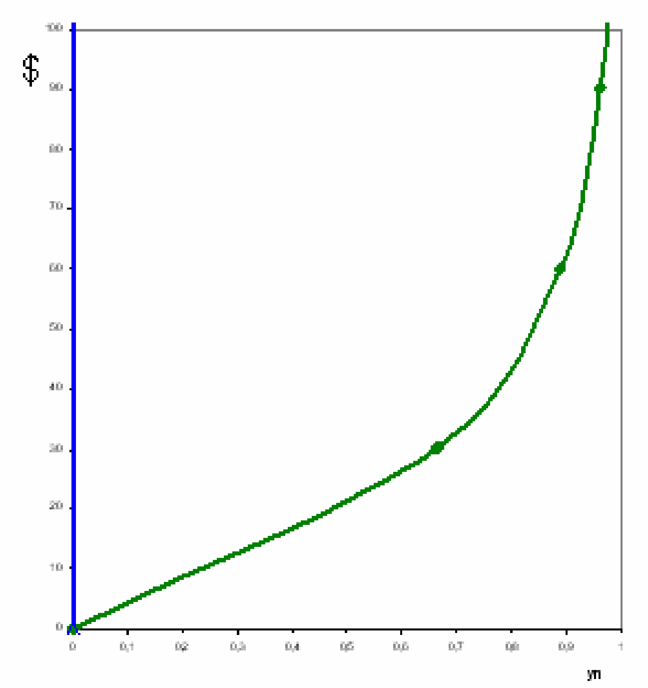

Figure 2: Cost curves for bound of lime

3 Experimental part

3.1 Determination of the adsorption coefficients *A*, *B*

Hide was ground and several samples of a known weight were immersed into pure water, every sample in a different volume of water. When the equationuilibrium was reached, the content of calcium oxide was estimated in both the pure solution (received by filtration or centrifugation) and in the solid sample. For the determination of calcium in solutions we used an atomic absorption method with the use of the Perkin Elmer Model 5000 Atomic absorption spectrophotometer. The experimental and calculated data using non-linear regression analysis are presented in the Table 1

The results of the non-linear regression calculation are the values of the adsorption coefficients of the isotherm: $A = 663;\ B = 57400 cm^3 g^{-1} = 57{,}4 m^3 kg^{-1}$

3.2 Determination of the effective diffusion coefficient of lime in hide

Experimental kinetics of the white hide washing we measured by putting a piece of the white hide into a vessel containing pure water for holding the white hide. We took away small quantities of water solution of lime in adequation time intervals to measure by the atomic absorption the concentration of lime as CaO g/cm^3.

Table 1: Experimental and calculated data of adsorption isotherm

C_0 (g cm^{-3}) 10^6	C_A (g cm^{-3}) 10^3	C_A (g cm^{-3}) calculated 10^3
39,3	7,79	8,0
24,8	7,82	6,78
19,8	4,44	6,15
13,0	6,62	4,94
9,66	3,51	4,12
7,98	5,30	3,63
7,42	2,92	3,45
6,90	1,96	3,28
6,44	2,95	3,12

For such small concentrations we can accept the assumption which is stated in Crank's book "Diffusion in polymers"[1] and can therefore solve the value of the effective diffusivity from the dependence of the concentration of lime outside the white hide on the square root of time.

$$\frac{m_\tau}{m_\infty} = \frac{4}{2b}\sqrt{\frac{D\tau}{\pi}} \qquad (1)$$

But $m_\tau = V_0 C_0$ and $m_\infty = \frac{V_0 C_p}{Na}$ and

$\frac{m_\tau}{m_\infty} = \frac{CoNa}{C_p}$ from the (1) we receive

$$D = \frac{tg^2(\alpha)(2b)^2 \, Na^2 \pi}{16} \qquad (2)$$

3.3 Experimental data

Weight of hide = 28,6 g, thickness 2b = 7 mm, volume of deliming 5% ammonium sulphate solution V_0 = 400 cm^3

$$Na = \frac{400}{28,6} = 13,986 \sim 14$$

Initial concentration of lime C_p = 5,1x10^{-3}g CaO/cm^3

Kinetics data of deliming process are shown in the Figure 2. By inserting the late value into the (2) we receive:

$$D = \frac{1,79^2 \times 10^{-6} \times 49 \times 10^{-6} \times 14^2 \times \pi}{16} \rightarrow$$

$$\rightarrow 6 \times 10^{-9} m^2 \min^{-1} = 10^{-10} m^2 s^{-1}$$

4. Conclusion

Costs curves, cost dependence on the deliming effectiveness are shown in the Figure 3, for the non-chemical (blue curve) and chemical deliming processes (green curve). Points on the curves represent the unit decanted cycles. The practically zero effectiveness of the non-chemical deliming results from the small initial concentration of lime in hide, which is approximately 0,5%; that means the process is found in an almost linear part of an adsorption isotherm, where the fixing power of lime on collagen surface is very strong. It is necessary to note and remind that the validity of our mathematical simulations is a limited acceptance of presumptions on which the equations were derived. The most important is the assumption that the diffusion process is not controlled or during the programmed time equilibrium is reached. (Fourier's diffusion number is about 1).

References:

[1] Crank, J. The Mathematics of Diffusion. Clarendon Press, Oxford, Second Edition, 1975

[2] Nernst, Z. Physics. Chem., 2, 613, 1888

[3] Kolomazník, K.; Janáčová, D. & Prokopová, Z.; *Modeling of Raw Hide Soaking*. WSEAS Transactions on Information Science and Applications.11(2),4.1994-1998. Athens, Greece, WSEAS. 2005, ISSN 1790-0832

[4] Janáčová, D., Kolomazník , K., Vašek, V., Mokrejš, P.: Mathematic *Modeling of Biology Changes in the Cured Hides Soaking*, , WSEAS Transactions on Systems, Australia, 2007, ISSN 1790-5117

[5] Janáčová, D. Kolomazník, K. & Vašek, V. et. al.;*Washing Processes Optimization*. In International Union of Leather Technologists and Chemists Societes. Centenary Congress. London, 1997

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