DELIMING OF UN-BONDED AND BONDED LIME FROM WHITE HIDE*

by

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ABSTRACT

The optimization of the white hide deliming operation was studied. Generally, white hide contains both non-bonded and various amounts of strongly bonded lime. Initially, the processing costs of the deliming of non-bonded lime are relatively low. However, at a certain stage of the deliming process the processing costs begin to increase rapidly because of the strength of the lime bound to collagen, and at this point it is suitable to interrupt the washing with pure water and replace it with a deliming agent. Our paper, with the use of a mathematical-physical process model, offers a solution as to when the interruption should be done. Experimental determinations of sorption isotherm, as well as the effective diffusion coefficients are presented. The above mentioned parameters, economical and technological, serve as input data for a computer program.

ABSTRACTO

Dentro de la optimización de la operación de desencale de pieles en tripa, el lavado con agua pura tanto como el proceso con químicos deben ser considerados. En general, piel en tripa contiene cal no fijada y en varios estados de fuerte fijación. Los costos de desencalar la cal no fijada son relativamente bajos, pero con la mermada concentración de cal en la piel estos suben, porque la intensidad de la fijación de la cal aumenta. A cierto estado en el proceso de desencale, los costos del proceso empiezan a aumentar en extremo y en ese punto es adecuado interrumpir el proceso de lavado con agua pura y reemplazarla con un agente desencalante. Nuestra publicación, con el uso de un modelo físico-matemático del proceso, da la respuesta de cuando la interrupción debe efectuarse. Determinaciones experimentales de la absorción isotérmica, como también los coeficientes efectivos de difusión son presentadas. Los mentados parámetros, tanto económicos como tecnológicos sirven como alimentación de datos a un programa de computador.

INTRODUCTION

Unhaired hide is strongly alkali as a result of employing sodium sulphide and lime in the unhairing process. The alkalinity of the hide has to be decreased because the subsequent processes are carried out under acid conditions. These 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. Due to its strong bond with collagen protein, the remaining lime is eliminated with the use of auxiliary deliming chemicals. Therefore weak acids or acidic salts, preferable divalent ones, are used. Boric acid, ammonium sulphate, sodium bisulphate and very recently sodium bicarbonate[1] or carbon dioxide[2] and magnesium lactate[3] have, in practice, been shown to be effective. A most important point is that the float should be as short as is feasible to obtain the highest concentration possible of the neutralizing agents. These chemicals can be offered in excess without causing acid swelling, unlike depickling, carried out with sodium carbonate, sodium sulphate, sodium polyphosphate, or other similar compounds[4], and in the presence of salt to prevent swelling during the first stage, where the pickled pelt comes in contact with water. Deliming is a special case insofar as the calcium ion is bound to connective tissues more firmly than mono-valent cations. The liberation of calcium from the protein is slower and more incomplete than it is for other cations. In practical tanning it has been observed that the bating process is always capable of liberating an additional amount of calcium[5]. Deliming agents break bonds between lime and collagen protein, resulting in neutral salts.

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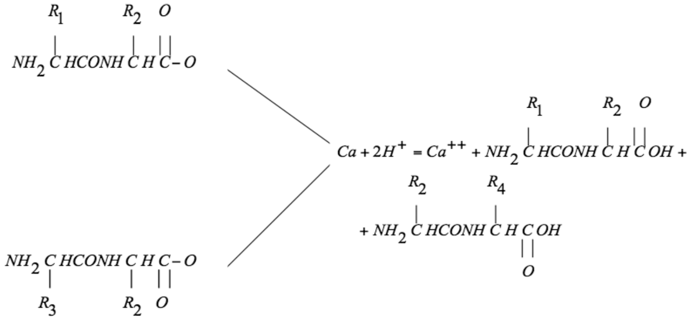


There exist many acid-reacting chemicals that are able to perform the chemical deliming process. Nowadays, environmentally friendly criteria should be applied to the selection of these chemicals. Unfortunately, most of the environmentally friendly deliming agents are more expensive than those used until 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 involves both plain washing with pure water and chemical processing. The main goal is to determine 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. Our paper, with the assistance of a mathematical-physical process model, gives the answer to the above mentioned question.

THEORY

The exact mathematical model of the processes, especially of the chemical deliming, is quite 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 ***(m$_s$)***:

$$y = \frac{m}{m_s} = \frac{C_0V_0}{C_sV} = \frac{C_0}{C_s}Na \qquad \text{eq. (1)}$$

C_0 - concentration of lime in deliming solution or in water, C_S - total initial concentration of lime in white hide, V_0 - volume of deliming solution or water, V - volume of white hide (load of drum), Na = V_0/V- soaking number, a dimensionless parameter which relates to the consumption of water or aqueous solutions of deliming agents. As mentioned in the introduction, calcium hydroxide is partly bonded to a collagen matrix. Quantitative description of the named bonds is given by sorption isotherm, *i.e.* the dependence of adsorbed lime concentration on the free lime concentration in the equilibrium. In most cases, Langmuir's isotherm is used:

$$C_A = \frac{AC}{1+BC} \qquad \text{eq. (2)}$$

where A and B are adsorption coefficients, being the former independent of the concentration.

For very small concentration (C), we can neglect the member BC in the denominator and eq. 2 becomes linear:

$$C_A = K.C \qquad \text{eq. (2a)}$$

It is valid K~A in the linear part of Langmuir's isotherm, while K equals the gradient of sorption isotherm in the given point (see eq. 3).

$$K = \frac{dC_A}{dC} = \frac{A}{(1+BC)^2} \qquad \text{eq. (3)}$$

The Fourier's number (dimensionless time) [***Fo***] is an essential parameter in the present modeling and it is defined by equations (3a) and (3b). Its value will determine whether the diffusion process is stable (time independent) or not (Crank, 1975).

$$Fo = \frac{k\tau}{b^2} \qquad \text{eq. (3a)}$$

$$k = \frac{D}{1+K} \qquad \text{eq. (3b)}$$

where D - effective diffusion coefficient of lime or neutral calcium salt (chemical deliming) in white hide, b - half thickness of white hide, τ - processing time. Collagen bonds are broken in the case of chemical deliming as a result of neutralization reaction and therefore $A = 0$ and according to eq. (3) and (3b) $K = 0$ and $k = D$.

Parameter ***k*** in eq. (3b) is a modified adsorption coefficient which can be estimated from the adsorption isotherm, *i.e.* the dependence of adsorbed lime concentration (***C$_A$***) in hide and on the free solution lime concentration ***C*** in the equilibrium conditions.

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.

$$N_{iN} = P\tau_{iN}K_E + K_vV_{oi} \qquad \text{eq. (4)}$$

$$N_{iCH} = P\tau_{iCH}K_E + K_{CH}V_{oi} \qquad \text{eq. (5)}$$

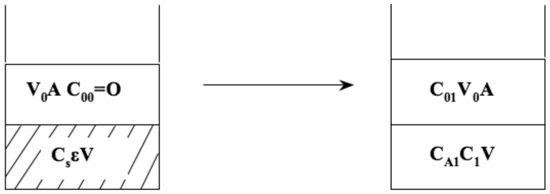
$$N_N = \sum_{i=1}^{n} N_{iN} \quad \text{eq. (4a)} \quad / \quad N_{CH} = \sum_{i=1}^{n} N_{iCH} \quad \text{eq. (5a)}$$

By combination of eq. (1), eq. (2), eq. (3), eq. (3a) and eq. (3b) we received the operation times of deliming process:

$$\tau_{iN} = \frac{b^2\left[\left(1+BC_i\right)^2 + A\right]}{D\left(1+BC_i\right)^2} \qquad \text{eq. (6)}$$

$$\tau_{CH} = \frac{b^2}{D} \qquad \text{eq. (7)}$$

Deliming degree calculation
a) *Non-chemical deliming*
Step 1. balance equation:



eq. (8)

$$C_SV = C_{01}V_{01} + C_1V_1 + VC_{A1}$$

By employing eq. (2) and using $C = \varepsilon C_0$ we get:

$$C_SV = C_{01}V_{01} + V\varepsilon C_{01} + \frac{A\varepsilon C_{01}V}{1 + B\varepsilon C_{01}} \qquad \text{eq. (9)}$$

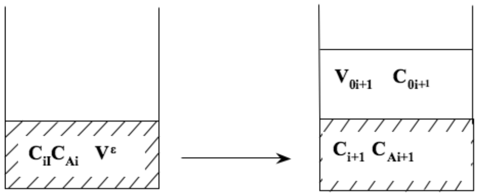
By solving eq. (9) we receive:

$$C_{01} = \frac{\varepsilon C_SB - Na_i - \varepsilon A - \varepsilon + \sqrt{\left(\varepsilon C_SB - Na_i - \varepsilon A - \varepsilon\right)^2 + 4C_SP}}{2P} \qquad \text{eq. (10)}$$

Where

$$P = \varepsilon B\left(Na_i + \varepsilon\right) \qquad \text{eq. (11)}$$

Analogously for ***i*** and ***i+1*** step:



eq. (12)

$$\varepsilon C_{0i}V + \frac{\varepsilon C_{01}AV}{1 + \varepsilon BC_{0i}} = C_{0i+1}V_{0i} + V\varepsilon C_{0i+1} + \frac{\varepsilon C_{0i+1}AV}{1 + \varepsilon BC_{0i+1}}$$

Again, the solution of the eq. (12) gives:

$$C_{0i+1} = \frac{-Y_i + \sqrt{Y_i^2} + 4PY_i}{2P} \qquad \text{eq. (13)}$$

Where

$$Y_i = Na_i + \varepsilon + A\varepsilon - X_iB\varepsilon \qquad \text{eq. (14)}$$

And

$$X_i = \varepsilon C_{0i} + \frac{A\varepsilon C_{0i}}{1 + B\varepsilon C_{0i}} \qquad \text{eq. (15a)}$$

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

$$y_N = \sum_{i=1}^{n} y_i = \sum_{i=1}^{n} \frac{C_{0i}V_{0i}}{V \cdot C_s} = \sum_{i=1}^{n} \frac{Na_iC_{0i}}{C_s} = \frac{1}{C_s}\sum_{i=1}^{n} C_{0i}Na_i \qquad \text{eq. (15)}$$

Nai = 1
for **i = 1,2,…, n**

b) *Chemical deliming*
Balance equations are the same, but ***A*** equals zero, resulting in $C_A = 0$.

$$C_sV = C_{01}V_{01} + \varepsilon C_{01}V \qquad \text{eq. (16)}$$

And

$$\varepsilon C_{0i}V = C_{0i+1}V_{0i} + \varepsilon C_{0i+1}V \qquad \text{eq. (17)}$$

From eq. (16) and eq. (17) follows:

$$C_{01} = \frac{C_s}{Na_1 + \varepsilon} \qquad \text{eq. (18)}$$

$$C_{0i+1} = \frac{\varepsilon C_{0i}}{Na_i + \varepsilon} \qquad \text{eq. (19)}$$

That means:

$$C_{02} = \frac{\varepsilon C_{01}}{Na_i + \varepsilon} = \frac{\varepsilon C_S}{\left(Na_i + \varepsilon\right)^2} \qquad \text{eq. (20a)}$$

$$C_{03} = \frac{\varepsilon C_{02}}{Na_i + \varepsilon} = \frac{\varepsilon^2 C_S}{\left(Na_i + \varepsilon\right)^3} \qquad \text{eq. (20b)}$$

And

$$C_{0i} = \frac{\varepsilon^{(i-1)}C_S}{\left(Na_i + \varepsilon\right)^i} \qquad \text{eq. (20)}$$

And for y_{CH}:

$$y_{CH} = \sum_{i=1}^{n} y_{CHi} = \sum_{i=1}^{\infty} \frac{Na_iC_{0i}}{c_p} = 1 - \left(\frac{\varepsilon}{\varepsilon + Na_i}\right)^n \qquad \text{eq. (21)}$$

because y_i are members of geometric sequence with quotient = $\dfrac{\varepsilon}{\varepsilon + Na_i}$

$Na_i = Na_1 = Na_2 = Na_3 \ldots\ldots Na_n$ are in the above equations and $c_i = \varepsilon C_{0i}$ are used. Using the equations eq. (3a), eq. (5), eq. (6), eq. (15) and eq. (21) 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 replacement by the chemical deliming operation.

EXPERIMENTAL

a) Determination of the Adsorption Coefficients A, B

White 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 equilibrium was reached, the content of calcium oxide was estimated in both liquid and solid phases of the sample. The equilibrium time was determined by a "blind" experiment; non-ground sample of white hide was immersed into water and in 2 hour intervals, the concentration of calcium ions in water was determined by atomic absorption. Practically, during 5 hours, the concentration did not change any more with time. With respect to the white hide ground sample, its concentration did not change remarkably within the first 5 hours. The pH is practically constant throughout the procedure so one can disregard the swelling of the hide. A Perkin Elmer Model 5000 Atomic Absorption Spectrophotometer was used to determine calcium content in both the solutions and white hide samples. The solutions could be aspirated directly (after dilution to the appropriate concentration), but the white hide samples needed to be first dissolved in hydrochloric acid (1:1) (approximately 1g in 10g of HCl) and then made up to volume in a 100ml volumetric flask. The experimental and calculated data using non-linear regression analysis are presented in Table 1.

TABLE I
Experimental and Calculated Data of Adsorption Isotherm

C_0 (g cm^{-3}) x 10^6	C_A (g cm^{-3}) x 10^3	C_A (g cm^{-3}) calculated x 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

The results of the non-linear regression calculation are the values of the adsorption coefficients of the isotherm:

$A = 663$; $B = 57400 cm^3 g^1 = 57.4 m^3 kg^1$

The adsorption coefficient A is dimensionless, *i.e.* the dimension equals 1.

Experimentally measured data of sorption isotherm are greatly dispersed. The required concentration changes are achieved by large volumes of solution in comparison to solid volume. In addition, relative errors are favoured by the rather small values of absolute concentrations. Also, the carbon dioxide present in the laboratory atmosphere might cause chemical deliming and thus negatively affect the measured data. The accuracy of the measurements can be also affected by the long time needed to reach equilibrium. Despite the above-mentioned inaccuracies we succeeded in the assessment of sorption coefficients. This enabled us to optimize the deliming process. Nevertheless, we are continuing to deal with the problem of determination of sorption constant and our results will be published in our next contribution.

b) Determination of the Effective Diffusion Coefficient of Lime in Hide

Experimental kinetics of the white hide washing was measured by putting a piece of the white hide into a vessel containing pure water with the equipment for holding the white hide. The liquid was stirred intensively, but the deformation of the piece did not happen. The volume ratio of water to white hide was higher than 500, so that the sampling of liquid (1 ml) did not affect the determined value of diffusion coefficient. We removed small quantities of the lime solution at different time intervals to determine by atomic absorption the concentration of lime as CaO g/cm^3.

Since the range of concentrations is low, one can assume the simplifications in the diffusion modelling reported by Crank[6] and solve the value of effective diffusivity according to external values.

$$\frac{m_\tau}{m_\infty} = \frac{4}{2b}\sqrt{\frac{D\tau}{\pi}} \qquad \text{eq. (22)}$$

where stands for the quantity of lime transferred from the white hide into the bath during the time *t* and *m* for the amount of lime to transfer from the hide to its surface in the equilibrium state. By applying mass balance, we receive:

$$C_s V = C_{0\infty} V_0 + C_\infty V$$

And from this - using $C_\infty = \varepsilon C_{0\infty}$ - we get:

$$C_\infty = \frac{C_s}{\frac{1}{\varepsilon} + Na}$$

Taking into account that in determination of the effective diffusion coefficient $Na + 1/\varepsilon$, it is possible to neglect $\frac{1}{\varepsilon}$ and we receive $C_\infty = \frac{C_s}{Na}$.

Since $m_\tau = V_0 C_0$ and $m_\infty = \frac{V_0 C_S}{Na}$ and $\frac{m_\tau}{m_\infty} = \frac{C_0 Na}{C_S}$

Plotting $\frac{m_\tau}{m_\infty}$ versus square root of time, a line is received and from its gradient ($tg\ \alpha$) it is possible to calculate the effective diffusion coefficient of non-bounded calcium hydroxide or calcium salts (sulphate) in hide using eq. 23.

$$D = \frac{tg^2(\alpha)(2b)^2 Na^2 \pi}{16} \qquad \text{eq. (23)}$$

Experimental data:

Weight of hide = 28.6 g
Thickness $2b$ = 7 mm
Volume of water V_0 = 400 cm^3
Na = $\frac{400}{28.6}$ = 13.986 ~ 14 (we suppose that density of hide is approximately 1g/cm^3)
Initial concentration of lime C_S = 5.1x10^{-3}g CaO/cm^3

$$tg(\alpha) = 1.85 \times 10^{-3} \min^{-\frac{1}{2}}$$

By inserting the late value into the eq. (23) we receive:

$$D = \frac{1{,}85^2 \times 10^{-6} \times 49 \times 10^{-6} \times 14^2 \times \pi}{16} = 6{,}33 \times 10^{-9} m^2 \min^{-1} \cong 10^{-10} m^2 s^{-1}$$

The value of the diffusion coefficient of calcium hydroxide in the infinite dilute water calculated from Nerst's equation[7] is 1.8 x 10^{-9} m^2 s^{-1}

$$D_0 = 8,931\cdot 10^{-10}\, T\left(\frac{l_+^0 l_-^0}{l_+^0 + l_-^0}\right)\frac{(z_+ + z_-)}{z_+ \cdot z_-}$$

from[8]

$$l_+^0 = 59.5; l_-^0 = 198.6$$

We chose $T = 293\ K$

Lower value of the measured diffusion coefficient in comparison with the value calculated from the Nerst's equation valid for limitary zero concentration is probably caused by Knudsend's diffusion.

DISCUSSION

Costs curves and cost dependence of the deliming effectiveness are shown in the Fig. 2 and Fig. 3 , both for the non-chemical (▲) and chemical (♦) deliming processes. Points on the curves represent the unit decanted cycles.

Fig. 2 indicates that only the chemical deliming process is effective for the presented parameters. They are:

Sorption coefficient A (fixing power of lime on a collagen surface) = 663
Sorption coefficient B = 57m^{3}kg^{-1}
Initial concentration of lime in hide C_p = 5,1kgm^{-3} ~ 0.5%
Hide thickness $2b$ = 7mm
Hide porosity ε = 0.5
Soaking number Na = 1
Effective diffusion coefficient of lime D = 10^{-10}m^{2}s^{-1}
Unit price of washing water K_V = 1 USD m^{-3}
Unit price of chemical deliming solution K_S = 30 USD m^{-3}
Input power of drum electric motor P = 15kW
Unit price of electric power K_E = 0.1 USD (kWh)$^{-1}$
Load of hide in drum V = 10 m^3 ~ 10 t

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 Fig. 3. 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 Fig. 3.

It is important to note and to remember 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).

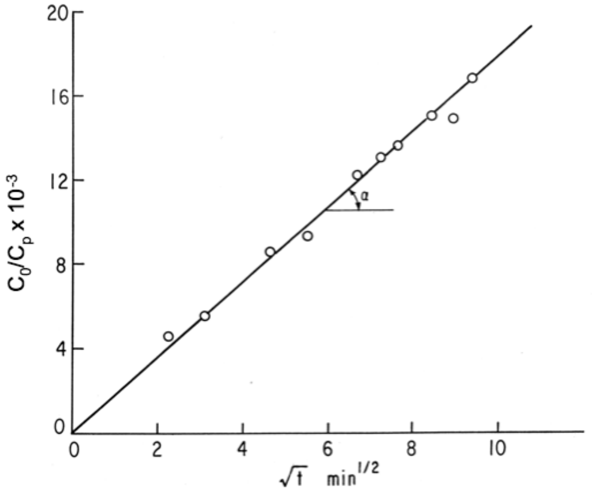


Figure 1. Determination of effective diffusivity of lime in white hide

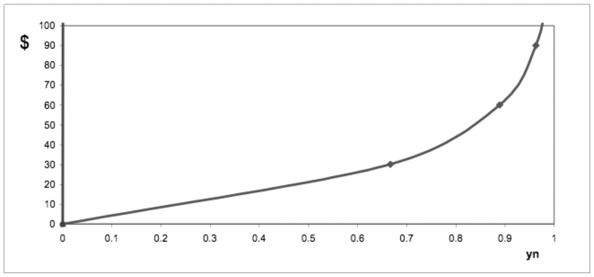


Fig. 2 Cost curves (non-chemical data lies on the ordinate)

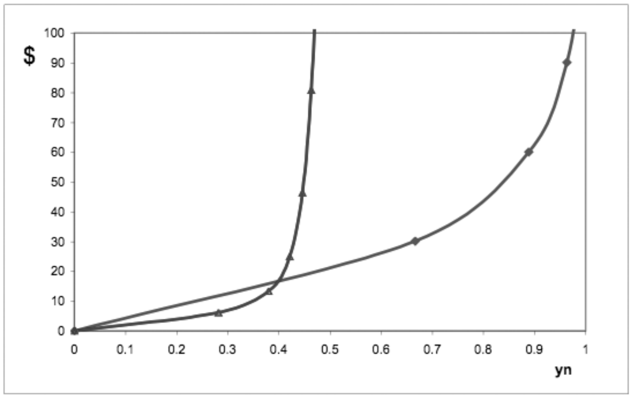


Fig. 3 Cost curves

CONCLUSION

The main purpose of this manuscript was again to demonstrate the purposefulness and usefulness of mathematical simulation for optimization of tanning processes. As shown in our previous article[9], the specific optimum cross-section point dividing chemical and non-chemical deliming depends on the specific input data for the computer program, i.e. sorption coefficients of Langmuir isotherm (A, B), initial concentration of lime (c_p), hide thickness (2b), hide porosity (ε), soaking number (Na), effective diffusion coefficient (D), unit price of washing water (K_V), unit price of chemical deliming solution (K_S), input power of drum electric motor (P) and unit price of electric power (K_E) and load of hide in drum (V)

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LIST OF SYMBOLS

C_0	concentration of lime in deliming solution or in water	[kg m^{-3}]
C_p	initial concentration of lime in hide	[kgm^{-3}]
C_S	total initial concentration of lime in white hide	[kg m^{-3}]
V_0	volume of deliming solution or water	[m^{3}]
V	volume of white hide (load of drum)	[m^{3}]
Na	soaking number	
D	effective diffusion coefficient of lime or neutral calcium salt (chemical deliming) in white hide	[m^{2}s^{-1}]
b	half thickness of white hide	[m]
τ	processing time	[s]
F_o	Fourier's number	
A	adsorption coefficient	[1]
B	adsorption coefficient	[m^{3}kg^{-1}]
P	input power of electric motor	[kW]
τ_{iN}	i-step operation time for non-chemical deliming	[h]
τ_{iCH}	i-step operation time for chemical deliming	[h]
K_E	unit price of electric power	[USD(kWh)$^{-1}$]
K_V	unit price of water	[USD m^{-3}]
K_S	unit price of water solution of deliming agent	[USD m^{-3}]
V_{0i}	volume of water and deliming agent water solution	[m^{3}]
N_N,N_{CH}	total costs of non-chemical and chemical deliming processes	[USD]
ε	porosity of white hide	[1]
n	number of operation steps	
D_0	effective diffusion coefficient of calcium hydroxide in the infinite dilute water	[cm^{2} s^{-1}]
l_+^o	cationic conductance at infinite dilution	[mhos/equivalent]
l_-^o	anionic conductance at infinite dilution	[mhos/equivalent]
T	absolute temperature	[K]
z_+	valence of cation	
z_-	valence of anion	