

Mathematical Modeling of Chemical Delimiting and Simulation of Economical Parameters in Gelatin Production

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Abstract—

The paper deals with optimization of the calcimine delimiting process during production of food grade gelatin. This process is the most important step from chemical engineering and environmental protection standpoint during production of food gelatin. The main objective of the paper is to provide a suitable mathematical description of the chemical delimiting process. The proposed model is subsequently used for optimization of the delimiting process to minimize the operating costs and environmental burden. The experimental part follows two main aims: determination of the effective diffusion coefficient of calcium sulfate during delimiting with ammonium sulfate based on experimentally measured data, and computer simulations of the operating costs from the viewpoint of various soaking numbers, degree of the delimiting and strength of the bond of calcium hydroxide to collagen. The results give ground for further optimization and exact transfer of laboratory data into real industrial operations.

Keywords— Limed collagen splits, gelatin production, chemical delimiting, mathematical modelling.

I. INTRODUCTION

Limed collagen splits (hereafter referred to as calcimine) is one of the major raw materials for food grade gelatin production. It is generated by the leather industry as a by-product of the liming operation. After removal of the excess sodium sulfide, calcimine is passed to a processing plant where it is subjected to re-liming the purpose of which is mainly removal of non-fibrous proteins and reduction of molar mass. The liming operation takes from 2 to 6 weeks, depending on the raw material and temperature.

As soon as the liming is finished it is necessary to remove

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practically all calcium hydroxide or possibly calcium carbonate. This is achieved by two subsequent steps, washing in plain water and then delimiting with the use of a delimiting chemical. Washing with plain water leads to dissolving of non-bonded and partial desorption of chemically bonded calcium hydroxide; in practice, substantial part of calcium hydroxide is removed from the surface and the inter-fiber space of calcimine. The amount of calcium hydroxide that can be removed by plain washing depends on the thickness of the calcimine used, the properties of washing water, temperature of the bath and time of the washing.

The course of the washing process can be also influenced by the process design [1], which can be industrially performed as:

- washing in a bath - the solid phase is dipped into a larger amount of washing liquid in only one washing cycle. The liquid does not flow in or out the bath during the process
- decantation washing - smaller volumes are used than in the previous case and the washing liquid is changed during several washing cycles
- through-flow washing - the washing liquid is continually fetched in and taken from the bath while the solid phase remains in the washing drum during the entire process. Through-flow washing is influenced by the volume of the washing liquid present in the drum.

However, the washing is not able to remove all the calcium hydroxide from calcimine; in other words, the operation comes to a critical point when no more calcium hydroxide can be removed and further washing is not efficient and thus economical (Fig. 1).

Calcium hydroxide dissolves better in cold water. However, calcimine is rather stiff in cold water and also swollen, which leads to “entrapment” of calcium hydroxide among the calcimine fibers, therefore it is advantageous to use tepid water. Temperature of 25°C has been reported as suitable [2].

The remaining calcium hydroxide, which is bonded to collagen in the form of calcium collagenate, can only be removed with chemical delimiting - washing with a solution of a delimiting agent. The principle of chemical delimiting lies in neutralization of calcium hydroxide with acids, some acid salts [2] and such delimiting agents that form with calcium ions salts soluble enough not to settle in the hide/calcimine mass [3]. From the viewpoint of the delimiting agent used, we distinguish two main types of chemical delimiting:

1. deliming with suitable acid salts
2. deliming with acid solutions

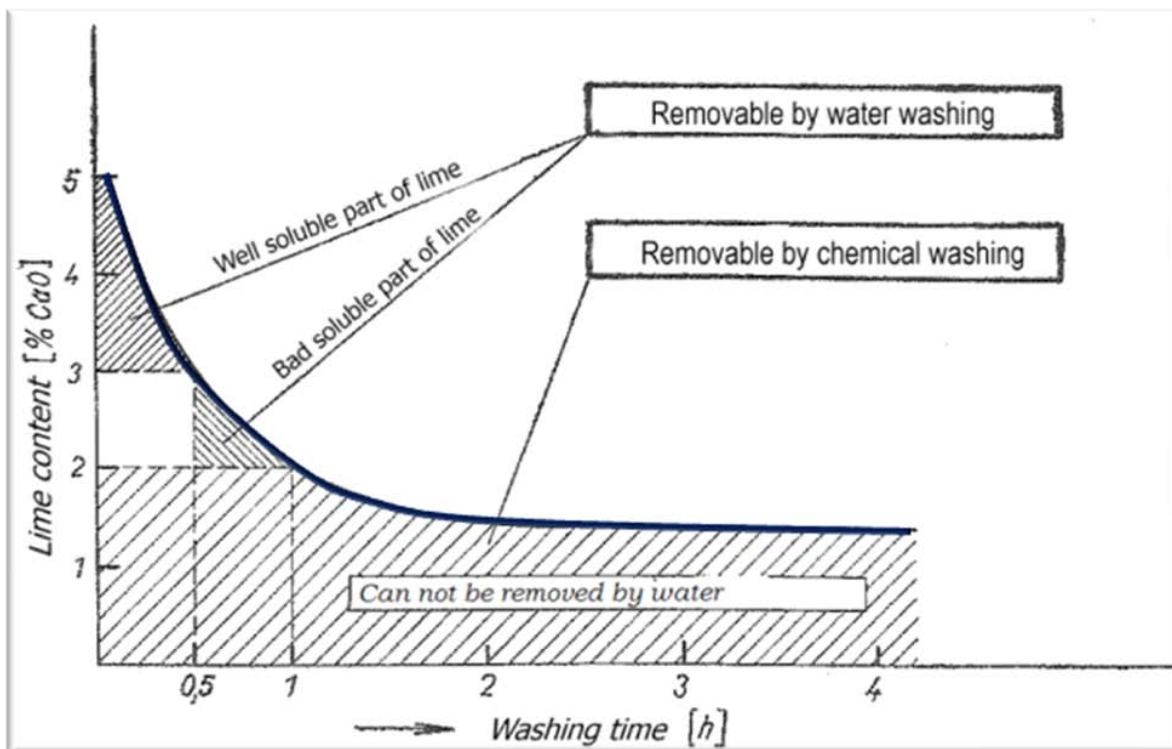
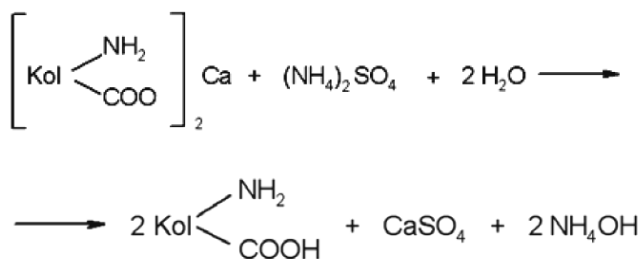


Fig. 1 Curve of lime extraction with water.

From the viewpoint of their deliming effect, ammonium salts of strong acids are considered to be most efficient, having the following advantages [2].

- react rapidly with calcium hydroxide
- buffer pH values in moderately alkaline area
- produce high and regular swelling of collagen fibers.

Generally, the insoluble calcium collagenate reacts with the deliming agent and a soluble calcium salt is formed which is then removed by washing in plain water. Mechanism of their action can be described by the following scheme:



However, deliming with ammonium salts also brings serious environmental issues, the most discussed of which is pollution of waste water with nitrogen compounds. To meet the limits for the maximal concentration of nitrogen compounds, these waters must be intensively treated by biological methods using nitrification and denitrification. Extensive research is being

carried out for non-ammonia deliming methods [4], with varying degrees of economical viability. Another approach is to orient the research also to optimization of the currently most frequently used deliming methods.

There are very few reports on the use of theoretical tools of chemical engineering for optimization of the real technological deliming procedure on industrial scale, especially from the viewpoint of the implementation of transport phenomena theory describing diffusion of low-molecular substances in natural polymers [5,6,7].

There are two main goals from the chemical engineering standpoint. At first, we have to find the optimum time, when to interrupt washing by water and replace it by chemical deliming. In order to do this, we express consumption of water for plain washing and concurrently the consumption of water solution of deliming chemical for chemical deliming. Both consumptions are expressed economically as a price of water and deliming chemical. By plotting of these prices against deliming efficiency we receive cost curves.

Since calcimine deliming is one of the key operations in calcimine processing into gelatin, the aim of this contribution is detailed mathematical description of the chemical deliming process with the use of the theory of transport phenomena, as well as determination of the transport parameters, namely the diffusion coefficient of the formed soluble calcium salt.

II. THEORY

A. Mathematical model of the transport of reacting components during chemical delimiting of calcimine

The authors of [8] analyzed the pre-tanning processes (particularly white hide delimiting) and stated in their results that for the mathematical description of these processes it is possible to apply some models known from the heterogeneous reaction kinetics. In the case that the determining step in particular technological process is the inner transport of the active component, we can use the “continuous reaction” model [9]. In cases where the transport process is accompanied by a chemical reaction we can apply the “non-reacted nucleus” model [9]. Since chemical delimiting with both acid solution and acid salt represent the latter case, the mathematical models of the transport of the reacting agents are based on the “non-reacted nucleus” model. The models are represented by the following systems of equations (1 and 2) and initial and boundary conditions (1a-f and 2a-f).

B. Diffusion of the acid (index i)

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

$$c_{pi} \frac{\partial x_m}{\partial \tau}(\tau) = \frac{1}{2} D_i \frac{\partial c_i}{\partial x}(x_m, \tau) \quad (1a)$$

$$V_0 \frac{\partial c_{i0}}{\partial \tau}(\tau) = -D_i S \frac{\partial c_i}{\partial x}(b, \tau) \quad (1b)$$

$$c_i(x_m, \tau) = 0 \quad (1c)$$

$$c_i(b, \tau) = \varepsilon c_{i0} \quad (1d)$$

$$c_i(x, 0) = 0 \quad 0 < x < b \quad (1e)$$

$$c_{i0}(0) = c_{i0p} \quad (1f)$$

Transport of the reacting components is graphically expressed in Fig. 2.

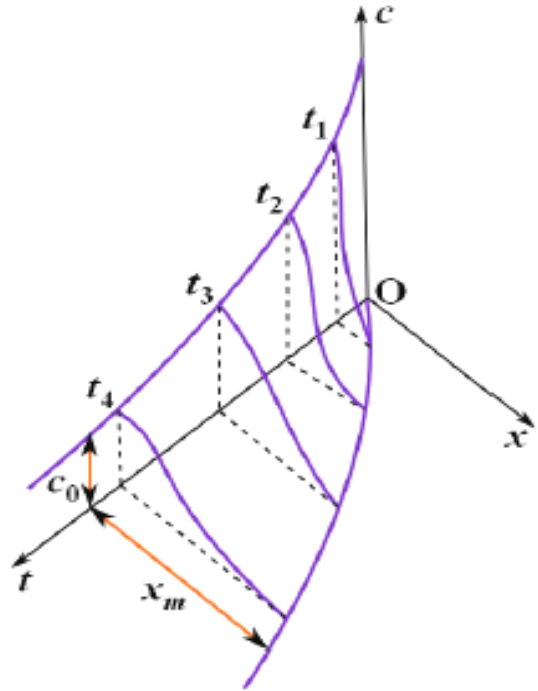


Fig. 2 Concentration field of the delimiting agent (acid) in the solid phase (calcimine).

C. Diffusion of the calcium salt (index j)

$$D_j \frac{\partial^2 c_j}{\partial x^2}(x, \tau) = \frac{\partial c_j}{\partial \tau}(x, \tau) \quad x_m < x < b \quad \tau > 0 \quad (2)$$

$$c_{pj} \frac{\partial x_m}{\partial \tau}(\tau) = \frac{1}{2} D_j \frac{\partial c_j}{\partial x}(x_m, \tau) \quad (2a)$$

$$V_0 \frac{\partial c_{j0}}{\partial \tau}(\tau) = -D_j S \frac{\partial c_j}{\partial x}(b, \tau) \quad (2b)$$

$$c_j(x_m, \tau) = c_{jp} \quad (2c)$$

$$c_j(b, \tau) = \varepsilon c_{j0}(\tau) \quad (2d)$$

$$c_j(x, 0) = 0 \quad (2e)$$

$$c_{j0}(0) = 0 \quad (2f)$$

Transport of the reacting components is graphically expressed in Fig. 3.

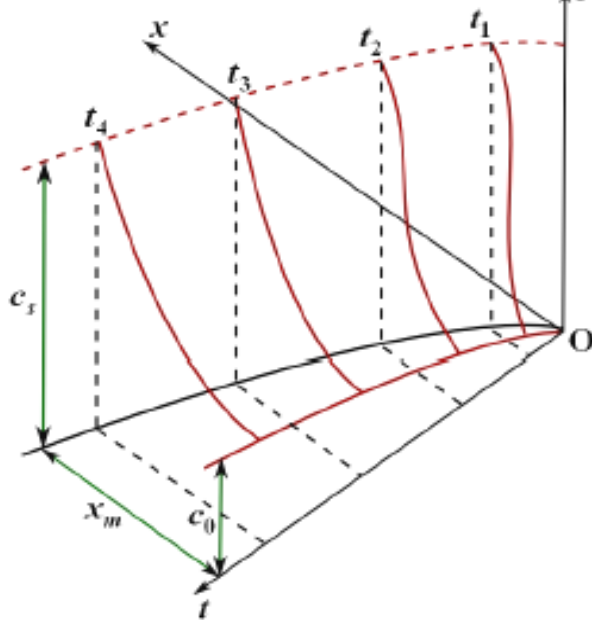


Fig. 3 Concentration field of the calcium salt washing-out from the solid phase (calcimine).

D. Determination of the effective diffusion coefficients

Determination of the effective diffusion coefficients proceeds from evaluation of the experimental data. Providing that the values of effective diffusion coefficients are very small, the dependence of the dimensionless concentration of the monitored substance on the square root of time is linear. For the determination of particular effective diffusion coefficients we used (3):

$$D_e = \frac{k^2 Na^2 c_{ps} b^2}{2c_R} \quad (3)$$

where k [$s^{-1/2}$] is the slope of the straight line of the dependence of c_0/c_p on the square root of time, Na [1] is the soaking number (ratio of the volume of washing bath to the volume of solid phase (calcimine)), c_{ps} [$kg \cdot m^{-3}$] denotes initial mass concentration of calcium hydroxide in calcimine, D_e [$m^2 \cdot s^{-1}$] stands for effective diffusion coefficient of calcium salt in calcimine, b [m] is half thickness of calcimine and c_R [$kg \cdot m^{-3}$] denotes the mass concentration of calcium salt saturated solution.

Theoretical value of the diffusion coefficient of calcium salt was estimated with the use of Nernst-Haskell equation for electrolytes at infinite dilution (4) [10]. This equation is sometimes stated in the form when expression R/F^2 is given its numerical value, i.e. 8.9×10^{-10} , and $l_+^0 + l_-^0 = \Lambda^0$ [11].

$$D_0 = \frac{RT}{F^2} \left(\frac{l_+^0 l_-^0}{l_+^0 + l_-^0} \right) \left(\frac{z_+ + z_-}{z_+ z_-} \right) \quad (4)$$

where D_0 [$cm^2 \cdot s^{-1}$] is diffusion coefficient of calcium salt at infinite dilution, R [$J \cdot mol^{-1} \cdot K^{-1}$] stands for the universal gas constant, F [$C \cdot mol^{-1}$] denotes Faraday constant, $l_+^0 + l_-^0$ [$S \cdot cm^2 \cdot mol^{-1}$] represent the limit ionic conductance for the

cations and anions, T [K] is the absolute temperature and z_+ , z_- [1] are the valences of cations and anions.

E. Operating costs

As explained above in the Introduction, non-bonded calcium hydroxide (either on the surface or in the calcimine inner volume) is removed by washing with plain water. Bonded calcium hydroxide is removed only partially, and further continuation if washing leads to enormous increase in operating costs because of extreme consumption of water. Optimization of the technology lies in determination of the point in which the washing process must be terminated in favor of chemical deliming. Using mathematical models of "non-reacted nucleus" and the sorption isotherm model [8], which is in our case represented by Langmuir adsorption isotherm, gives us the base for determination of that critical point.

For the economical optimization we choose the following function (5):

$$N_S = N_E + N_V \quad (5)$$

where N_S denotes the overall operating costs as a sum of the costs of the energy required for the operation of mechanical device N_E and N_V stands for the costs of the deliming washing liquid. Then the overall operating costs can be expressed by (6):

$$N_S = P \cdot \tau \cdot K_E + V_0 \cdot K_V \quad (6)$$

where τ stands for time [s], K_E is the unit price of electric power [$EUR \cdot kWh^{-1}$], V_0 is the volume of washing liquid [m^3] and K_V is the unit price of water [$EUR \cdot m^{-3}$].

III. EXPERIMENTAL

The experimental part comprises determination of the effective diffusion coefficient of calcium sulfate in the calcimine inner volume and the input data for the simulations of cost curves at various soaking numbers and for the determination of critical time when it is necessary to replace plain washing with chemical deliming.

A. Determination of the effective diffusion coefficient of calcium sulfate during deliming with ammonium sulfate

The following chapter shows determination of the effective diffusion coefficient of calcium sulfate during chemical deliming with aqueous solution of ammonium sulfate.

The principal of experimental work was the following: a sample of solid phase (calcimine) of a known thickness and volume was merged in the deliming bath of a given volume and stirred intensively. Samples of the liquid phase were taken after selected time periods (particularly after 5.02, 9.99, 19.98, 30.14, 39.94, 59.29, 60.06, 70.06, 79.92 and 90.06 min) and subjected to analysis. The concentration of calcium oxide was determined with the use of atomic absorption in aqueous solutions after mineralization in HNO_3 in cooperation with the Department of Polymer Engineering, Faculty of Technology,

Tomas Bata University in Zlin, according to the Czech ISO standard CSN ISO 7980. We assumed that the calcimine density was equal to the density of the delimiting solution. The volume of the samples was as small as possible so that the overall volume taken for analysis could be neglected in relation to the initial volume of the bath. The measurements were taken under the conditions listed in the following Table I.

Table I Input experimental data of the solid and liquid phases.

| Parameter | Value | Units |
|--|-----------------------|-----------------------|
| Weight of calcimine m | 15.047 | [g] |
| Calcimine density | 1000 | [kg·m ⁻³] |
| Average half thickness of calcimine b | 3.5 | [mm] |
| Temperature of the delimiting bath T | 26 | [°C] |
| Volume of the delimiting bath V_0 (360 ml H ₂ O + 60 ml of 5% solution of ammonium sulfate) | 420 | [cm ³] |
| Initial concentration of calcium hydroxide in calcimine c_p | 5.11×10^{-3} | [g·cm ⁻³] |
| Initial concentration of calcium sulfate in calcimine c_p | 12.4×10^{-3} | [g·cm ⁻³] |
| Solubility of calcium sulfate c_R [51] | 2.97×10^{-3} | [g·cm ⁻³] |

B. Optimization of washing and chemical delimiting

Simulation software has been developed that allows simulation of cost curves from different input data based on real industrial operations. The input data for the cost curve are provided in the following Tables II and III.

Table II Simulated calculation of the values of time and operating costs for various soaking numbers.

| Na | Time | Operating cost |
|------|----------|----------------|
| [1] | [s] | [EUR] |
| 3.0 | 10735.42 | 81.17 |
| 3.7 | 9798.24 | 77.16 |
| 4.4 | 9253.70 | 75.77 |
| 5.1 | 8896.48 | 75.63 |
| 5.8 | 8643.72 | 76.18 |
| 6.5 | 8455.30 | 77.17 |
| 7.2 | 8309.37 | 78.44 |
| 7.9 | 8192.97 | 79.90 |
| 8.6 | 8097.96 | 81.51 |
| 9.3 | 8018.92 | 83.22 |
| 10.0 | 7952.14 | 85.01 |

Table III Example of the input data for computer simulation of cost curves for various soaking numbers.

| Parameter | Value | Units |
|---|--------------------|------------------------------------|
| Volume of extraction agent* | 5 | [m ³] |
| Volume of calcimine* | 1 | [m ³] |
| Sorption constant** | 1 | [1] |
| Porosity | 0.5 | [1] |
| Half thickness of calcimine | 0.0025 | [m] |
| Diffusion coefficient | 1×10^{-9} | [m ² ·s ⁻¹] |
| Initial concentration of calcium hydroxide in calcimine | 28 | [kg·m ³] |

* These values are an example, their ratio (the soaking number, Na) was changing as shown in Table II.

** Sorption constant characterizes the bond strength of calcium hydroxide to calcimine (collagen).

IV. RESULTS AND DISCUSSION

A. Determination of the effective diffusion coefficient of calcium sulfate

The results of the measurement of the delimiting process in aqueous solution of ammonium sulfate are summarized in Table III.

Table III Results of the measurements for the calcimine delimiting in aqueous solution of ammonium sulfate.

| Measurement number | $\sqrt{\tau}$ [min ^{1/2}] | $c_0 \times 10^6$ [g·cm ⁻³] | $c_0/c_p \times 10^3$ [1] |
|--------------------|--|--|------------------------------|
| 1 | 2.24 | 21.34 | 4.18 |
| 2 | 3.16 | 34.63 | 6.78 |
| 3 | 4.47 | 51.07 | 9.99 |
| 4 | 5.49 | 61.56 | 12.05 |
| 5 | 6.32 | 62.61 | 12.25 |
| 6 | 7.07 | 58.07 | 11.36 |
| 7 | 7.75 | 78.71 | 15.40 |
| 8 | 8.37 | 76.61 | 14.99 |
| 9 | 8.94 | 77.31 | 15.13 |
| 10 | 9.49 | 79.05 | 15.47 |

The value of effective diffusion coefficient of calcium sulfate was calculated from the slope of the straight line obtained from the dependence of dimensionless concentration of calcium on the square root of time according to equation (2.3) (Fig. 4).

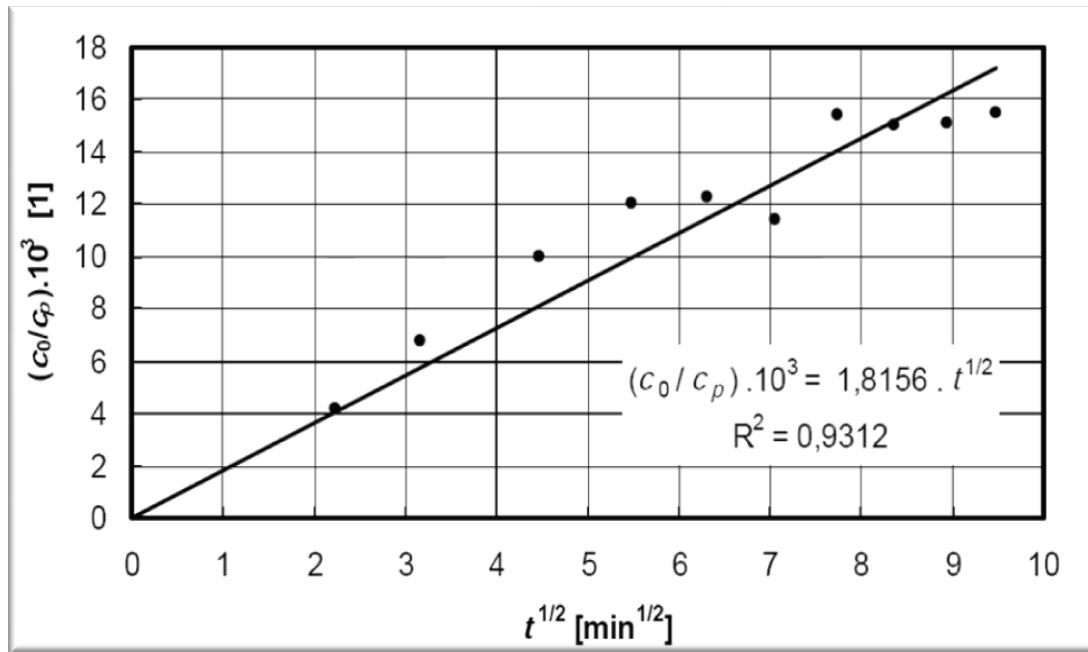


Fig. 4 Determination of the effective diffusion coefficient of calcium sulfate during deliming with ammonium sulfate.

After incorporation of the experimentally measured data we obtained the value of the effective diffusion coefficient of calcium sulfate of $1.10 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

$$D_e = \frac{k^2 Na^2 c_{ps} b^2}{2c_R} =$$

$$= \frac{(1.8156 \cdot 10^{-3})^2 \cdot 27.91^2 \cdot 12.4 \cdot (3.5 \cdot 10^{-3})^2}{2 \cdot 2.97 \cdot 60} =$$

$$1.10 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$$

Theoretical value of the effective diffusion coefficient calculated according to Eq. (2.4) is $9.11 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

$$D_0 = 8.931 \cdot 10^{-10} \cdot 299 \cdot$$

$$\cdot \left(\frac{59.5 \cdot 80}{59.5 + 80} \right) \left(\frac{2+2}{2 \cdot 2} \right) \cdot 10^{-4} = 9.11 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

The results show that the value of the effective diffusion coefficient characterizing the particular technological process does not differ significantly from the theoretical value at infinite dilution. We can assume that the reactions in heterogeneous area are accompanied with heat and mass transfer the parameters of which are independent on the reaction system construction. Experimental determination of

the effective diffusion coefficient is an important step because the value of the coefficient is one of the key input parameters for the cost curves in optimization of the deliming process.

B. Cost curve

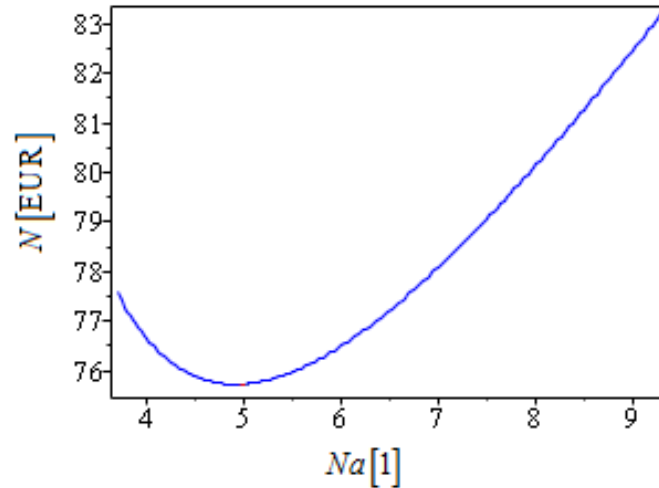
The input data for the simulation of the cost curves were the following (Table IV):

Table IV Input data for simulation of the cost curve.

| Parameter | Value | Units |
|----------------------------------|---------------------|------------------------------------|
| Strength of the chemical bond A | 50* | [1] |
| | 150** | |
| Sorption constant B | 57 | [1] |
| Soaking number Na | 1 | [1] |
| Initial concentration c_s | 5 | [kg·m ⁻³] |
| Calcimine half thickness b | 0.003 | [m] |
| Calcimine volume V | 10 | [m ³] |
| Diffusion coefficient D | 1×10^{-10} | [m ² ·s ⁻¹] |
| Unit price of water K_V | 1 | [EUR·m ⁻³] |
| Unit price of energy K_E | 0.1 | [EUR·kWh ⁻¹] |
| Unit price of the chemical K_C | 30 | [EUR·m ⁻³] |
| Input power P | 15 | [kW] |
| Porosity ε | 0.5 | [1] |

* First simulation

** Second simulation



The following Fig. 5 shows graphical expression of Table IV.

Fig. 5 Simulation of the cost curve in the delimiting process.

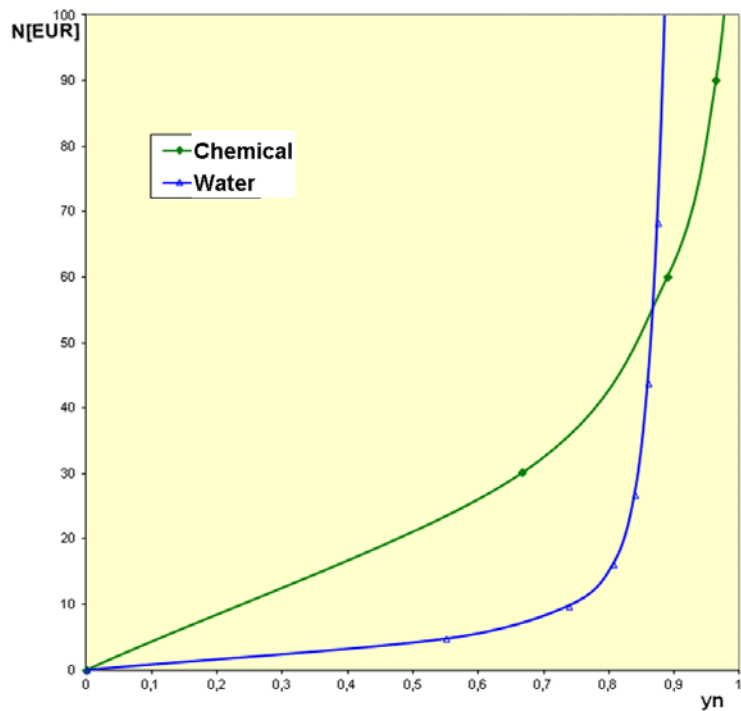


Fig 6 Dependence of the costs of water and chemical during delimiting on the delimiting degree (y_n) at the value of the bond strength $A=50$.

C. Optimal time for replacement of plain washing with chemical delimiting

As explained above in the Introduction, non-bonded calcium hydroxide (either on the surface or in the calcimine inner volume) is removed by washing with plain water. Bonded

calcium hydroxide is removed only partially, and further continuation of washing leads to enormous increase in operating costs because of extreme consumption of water.

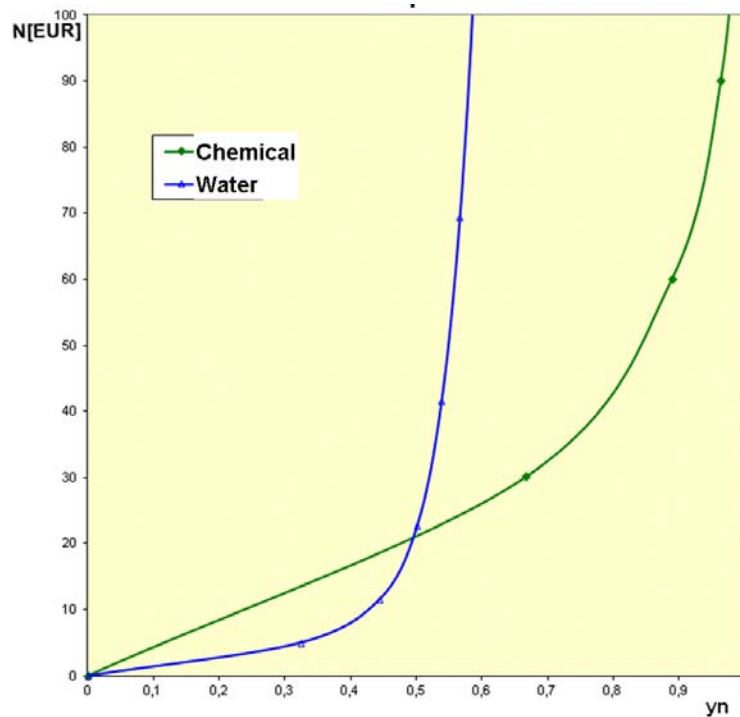


Fig 6 Dependence of the costs of water and chemical during delimiting on the delimiting degree (y_n) at the value of the bond strength $A=150$.

Optimization of the technology lies in determination of the point in which the washing process must be terminated in favor of chemical delimiting. Using mathematical models of “non-reacted nucleus” [12] and the sorption isotherm model [8], which is in our case represented by Langmuir adsorption isotherm, gives us the base for determination of that critical point. Figures 6 and 7 are graphical expressions of the data from the Experimental part. It is obvious from the figures that the higher the bond strength of calcium hydroxide to collagen (A increases from 50 to 150), the sooner (at lower delimiting degrees y_n) it is necessary to cease the washing with plain water and replace it with chemical delimiting.

V. CONCLUSION

Mathematical models based on the theory of transport phenomena and heterogeneous chemical reactions allow utilization of their limit solutions for the determination of effective diffusion coefficients of the delimiting agents (“non-reacted nucleus” model) and the formed neutralization salts (continuous reaction model). The experimentally determined effective diffusion coefficient shows acceptable accordance with the theoretical value at infinite dilution. Cost curves have been simulated for various soaking numbers and bond strengths. The results give ground for further optimization calculations and the design of suitable processing equipment for the optimal course of the reactions.

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