

AUTOMATIC CONTROL OF RECYCLING TECHNOLOGY FOR CHROMIUM FROM LIQUID AND SOLID TANNERY WASTE*

by

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ABSTRACT

A low cost computer-controlled system to recycle chromium containing liquid and solid waste from the tanning industry is described. The mathematical model for the recycling technology is based on the chemical-physical engineering description of the heterogeneous kinetics of the process. Regressive analysis was used to determine values for the parameters in each kinetic equation from experimental data. The idea for the recycling technology lies in using the reaction of non-environmentally friendly chromium containing liquid and solid wastes and creating new products that are not toxic and can be used in other industrial applications. The proposed model was used for a simulation test and for an optimum calculation in connection with minimum operating costs of the recycling technology. The process, including the computer control system, was demonstrated with laboratory equipment using real chromium-containing liquid and solid waste obtained from a beam house.

INTRODUCTION

At present, the problem is not the technological solution to processing and recycling chrome-containing tannery waste, but the economic aspects. Simple solutions such as disposal in open air or combustion have the hazard of oxidizing trivalent chromium compounds to carcinogenic hexavalent compounds.¹ For this reason, we focused on efficient and controlled dechromation technology. Proposed technologies of hydrolyzing chromium wastes chiefly produce relatively expensive protein hydrolyzates,^{2,3,4} even though they have comparable quality. Also inferior quality chrome sludge is produced whose processing into reclaimed tanning salt on large industrial scale has not been successful. It is thus obvious that successful implementation of laboratory-developed technology in industrial practice requires production of high-quality protein hydrolyzates and chrome

sludges of equal quality at low price. In order to meet these conditions, investment and operating costs have to be minimized. We worked out conditions for employing a current tanning drum for enzymatic dechromation of tanning waste.¹ The same drum is used as a rotating filter. After filtration, the chrome cake containing magnesium hydroxide that remains in the drum is used to remove chromium from spent liquor.⁵ This procedure reduced investment costs by approximately 90%. Concurrent dechromation of tanning wastewater removes chromium in both solid and liquid phases. Another result of the procedure we proposed and verified on an industrial scale is an increased chromium content in sludge, thus increasing probability of its successful use as a raw material for various applications. We optimized dechromation of spent liquor with a view to minimizing total operating costs, and computer-controlling the whole process in laboratory-monitored equipment.

EXPERIMENTAL

In the first stage we prepared a filter cake through enzymatic hydrolysis of chrome shavings in a tanning drum of 1.5 m diameter and 1 m width. After enzymatic hydrolysis we replaced the drum lid with a filter cloth and separated dilute protein solution. To the filter cake in the drum, we added spent liquor at a starting concentration of 2500 ppm chromium, ensuing decolorization of liquid occurred in 30 min and the content of chromium was 10 ppm as measured by atomic absorption. Residual filter cake consisting of 19% solid phase, 22% chromic oxide, 9% magnesium oxide on moisture-free basis was taken to the laboratory of our Institute and placed in a filter press. The suspended filter cake was transported by centrifugal pump from storage tank S3 (see Fig.1) to filter press. On filling that, we close valve EV3, opened valve EV1 and began filling measuring tank M. When the level in the measuring tank reached the required value, valve EV1 from storage tank of spent liquor was closed and both centrifugal pumps were switched on. In the course of the experiment, we measured chromic ion concentration with a photocell, i.e. performed experimental identification in a suitably chosen sampling period.

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Employing equation (6), we calculated the rate constant of precipitation reaction and according to relation (10) estimated optimal time. Reaching that, we opened valve on alkaline solution storage tank EV2 and measured necessary quantity of alkali to precipitate residual chromium for its concentration corresponding to optimal time. Once chromic ion concentration was virtually equal to zero (less than 5 ppm), the cycle was finished. After calculating magnesium oxide content, we either repeated the dechromation cycle or exchanged the filter cake in the filter press.

THEORY

To determine optimal time for dechromation of spent liquor, we assume filter cake is in the filter press through which solution of chromium ions circulates. The technological scheme is shown in figure 1. On attaining optimal time, the remaining content of chrome is precipitated with strong alkali, e.g. sodium carbonate or sodium hydroxide.

Total operating costs (N_T) are determined by the sum of costs of the power consumed by the electric motor of the centrifugal pump (N_E) and price of consumed alkali (N_A).

$$N_T = N_E + N_A \quad (1)$$

Cost of consumed power is determined by the product of the unit price of energy (K_E) in \$/kwh, motor input energy/time (P) in kw, and time (τ) in hours during which the centrifugal pump is in operation.

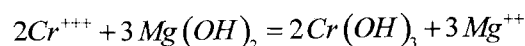
Cost of additional precipitation of chromic ions is proportionate to alkali unit price (K_A) \$/mole and the amount consumed (n_A) in moles.

$$N_T = K_E P \tau + K_A n_A \quad (2)$$

The quantity of moles used depends on molar concentration of residual chromium c in the spent liquor and the total volume of processed spent liquor (V).

$$N_T = K_E P \tau + K_A V c \beta \quad (3)$$

where β is the stoichiometric coefficient of the precipitating chemical. Reaction time and final concentration of chromic ions are affected by kinetics of precipitation reaction which proceeds in filter press according to following equation:



when $Mg(OH)_2$ is used for precipitating the chromium in the filter cake. To complete the precipitation of chromium,

sodium hydroxide is used for the reaction.

For analysis of the transport process, diffusion is excluded. The rate of the precipitation reaction is then:

$$-\frac{dc}{d\tau} = k_1 c_n^3 c^2 \quad (4)$$

where c_n is concentration of magnesium hydroxide in the filter cake. Due to the fact that we want the final concentration of chromium ions to be as small as possible in the spent liquor. We use such quantity of filter cake to have the content of magnesium hydroxide in substantial excess so that its concentration may be regarded as constant, thereby simplifying equation (4) to:

$$-\frac{dc}{d\tau} = kc^2, \quad \text{kde } k = k_1 c_n^3 \quad (5)$$

Integration of (5) gives:

$$\frac{1}{c} - \frac{1}{c_p} = k\tau \quad (6)$$

from where

$$c = \frac{c_p}{k\tau c_p + 1} \quad (7)$$

where c_p is starting concentration of chromic ions in spent liquor. Substituting equation (7) into equation (3), we obtain the total cost as a function only of time:

$$N_T = K_E \tau P + \frac{c_p V \beta K_A}{k\tau c_p + 1} \quad (8)$$

Figures 2a and 3 show the dependence of chief operating costs on time with given parameters of spent liquor volume (Figure 2a) and on the value of the precipitation reaction rate constant.

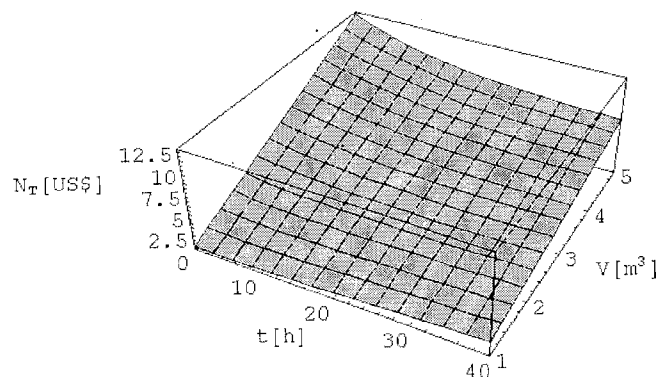
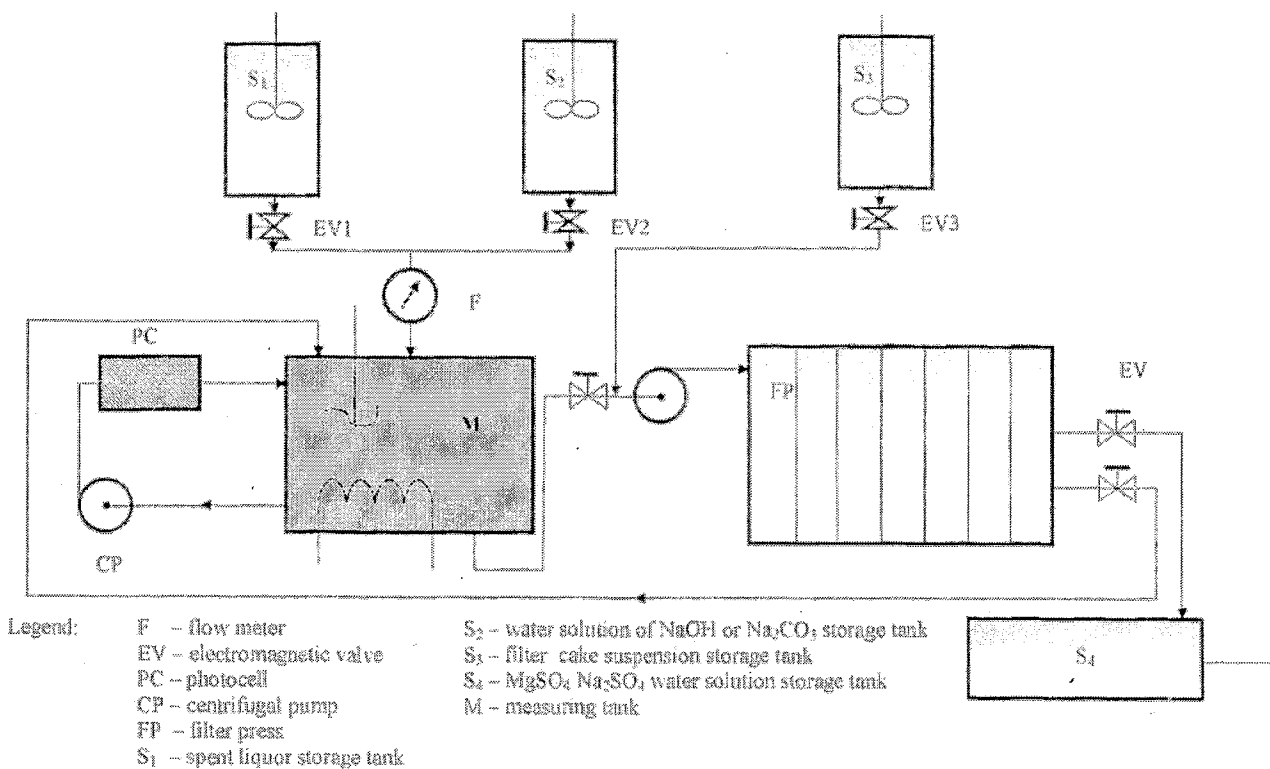


Figure 2a. - Dependence of the cost function on load of spent liquor

Optimal time is obtained through derivation of equation (8) by time, result is put equal to zero and thence optimal time is calculated.



Legend: F - flow meter, EV - electromagnetic valve, PC - photocell, CP - centrifugal pump, FP - filter press, S1 - spent liquor storage tank, S2 - water solution of NaOH or Na2CO3 storage tank, S3 - filter cake suspension storage tank, S4 - MgSO4 Na2SO4 water solution storage tank, M - measuring tank

Figure 1. - Dechromation of spent liquor

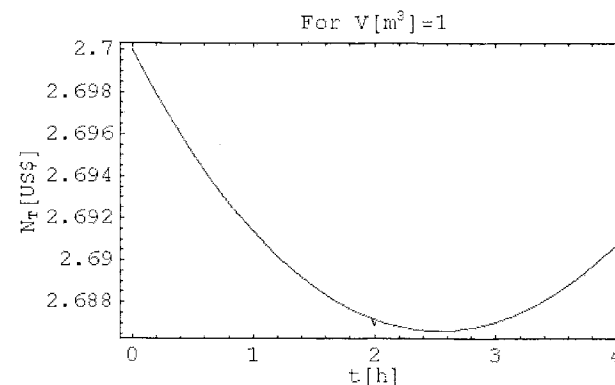


Fig. 2b. - Cost function

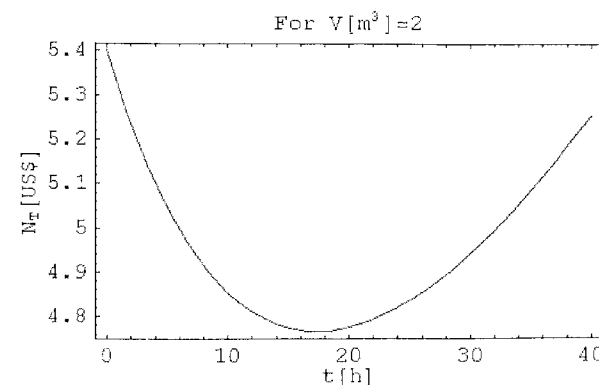


Fig. 2c. - Cost function

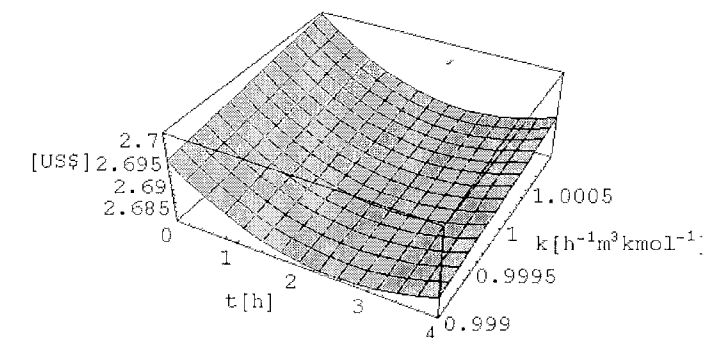


Figure 3. - Dependence of the cost function on velocity

$$\frac{dN_T}{d\tau} = K_E - \frac{c_p^2 V \beta k K_A}{(k\tau c_p + 1)^2} = 0 \quad (9)$$

From that

$$\tau_{opt} = \sqrt{\frac{V \beta K_A}{K_E k P} - \frac{1}{k c_p}} \quad (10)$$

Figure 4 exhibits the dependence of optimal time on volume of spent liquor and rate constant of the precipitation reaction (Figure 5).

DISCUSSION

Dependence of the main operating costs on time was modeled based on the following parameters:

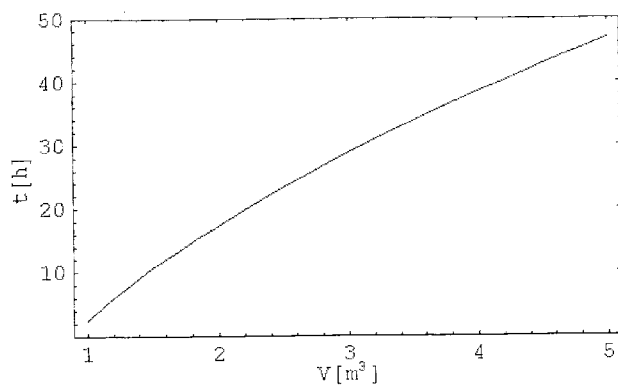


Figure 4. - Dependence of optimal time on spent liquor load

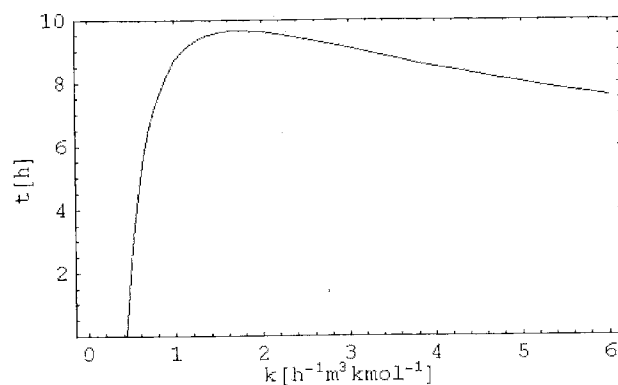


Figure 5. - Dependence of optimal time on speed constant

- unit price of power $K_E = 0.1$ US \$ kWh⁻¹
- electric motor input $P = 0.7$ kW,
- starting concentration of chromic ions $c_p = 0.06$ kmol m⁻³,
- unit price of alkali $N_A = 15$ US \$ kmol⁻¹,
- volume of processed spent tanning liquor $V = 1$ m³.

Figure 2a indicates the dependence of costs on time with a changing volume of processed liquor, and for a value of precipitation reaction rate constant $k = 0.5$ m³h⁻¹kmol⁻¹. The minimum for a volume of 2m³ is not too sharp but sharpness increases with decreasing volume of processed liquor. The tendency is clear when comparing Figures 2b' and 2c. The opposite results are obtained with constant volume ($V = 1$ m³) and constantly changing precipitation rate as experimentally identified parameters for controlling the recycling process (see Figure 3). The dependence of optimal time, i.e. at minimal operating costs, on volume of processed liquor is shown in Figure 4 and on value of precipitation rate constant in Figure 5. With very low levels of the rate constant, we even arrive at a negative time meaning that the proposed technology, for those starting parameters, becomes economically disadvantageous. An increasing rate constant is followed by a swift increase in the optimal time over the maximum. For further increases of k , a slow

decrease in time takes place when, at a limit for $k \rightarrow \infty$, the optimal time is zero. At time of zero, very fast dechromation of spent liquor occurs. This situation, however, differs greatly from low values of the rate constant at which, as has been said, the proposed dechromation process is uneconomical. Concrete model calculations are naturally valid for concrete input parameters. For a real process, real input parameters have to be specified.

SUMMARY

The chromium filter cake obtained after enzymatic digestion of chrome-tanned waste is used to precipitate chromium ions in spent liquor. Concentration of chromium ions in dechromed solid and liquid waste is controlled to minimize operating costs. The optimum operating time is determined by economic parameters (unit price of electrical energy and additional precipitants), technological parameters (volume of spent liquor and the initial concentration of chromium ions in spent liquor), and the kinetic parameter of the precipitation reaction in the filter cake (velocity constant). The whole process was monitored and computer-controlled in laboratory equipment.

ACKNOWLEDGMENTS

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LIST OF SYMBOLS

N_T	Chief operating costs	\$
N_E	Electric operating costs	\$
K_E	Unit price of electric energy	\$(kWh) ⁻¹
K_A	Unit price of alkali solution	\$(k mol) ⁻¹
P	Motor input	kW

n_A	Alkali moles consumed	k mol
τ	Time	h
c	Molar concentration of chromium in spent liquor	k mol m ⁻³
V	Volume of spent liquor	m ³
k	Speed constant	h ⁻¹ mol ⁻¹ m ⁻³

CONVENTION DISCUSSION

David Rabinovich, Jos. Lowenstein & Sons, Inc. - When precipitating chromium hydroxide with sodium hydroxide,

the pH is very critical. You can begin to redissolve since chromium is amphoteric. What guarantees do you have or what do you control to not to redissolve the chromium?

The pH of the spent liquor is approximately 4. The pH of the filter cake is about 9. Because we use excess magnesium hydroxide, the pH is approximately 9. The control is safe because we use sufficient content of magnesium in the filter cake and this provides safe control of the pH.