Control Recycling Technology of Tannery Chromium Wastes

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Abstract: - The leader industry produces several kinds of wastes. That is why is necessary to look for the technologies and methods to process these waste to the products unloading the living environment. The solving of the recycling technology for the liquid and solid chromium wastes is only one problem from this area. The importance exactly of this problem results from the fact, that the chromium tannery wastes are potential dangerous for the environment. In this contribution there is described mathematical model of the recycling process, proposal of the laboratory technological equipment for the total chromium recycling of the liquid and solid waste. For this laboratory equipment was solved the computer control system with the full control algorithm closed recycling technology according to optimal electrical energy and alkali solution consumption. Experimental laboratory model were built in the Department of Automatic Control Faculty of Applied Informatics Tomas Bata University in Zlín an apparatus fully equipped with sensors and actuators.

Key-Words: - Tanned waste recycling, Enzymatic hydrolysis, Simulation, Real–time, Process control, Microcomputer’s technique, control algorithms.

1 Introduction

Although the leather industry is environmentally important as a user of the by-product of the meat industry, it is perceived as a consumer of resources and a producer of pollutants. When processing one metric ton of raw hide, 250 kg of leather – the final product – is obtained and 600 kg of solid waste and 40,000 m3 of waste water is produced1. In order to reach the status of future sustainability, the industry must aim to reduce the consumption of chemicals, water and energy resources and to minimize the production of solid and liquid wastes. In other words, rationalisation has to be done.Progress can be actively aided in this manner, particularly in introducing automation, continualisation and robotisation of tanning operations[2,3,4]. The most serious problem and now under control, are chrome tanned wastes. The simplest solution for solid chrome tanned waste is its disposal in the open air. But such a solution is potentially dangerous, because no-control processes landed chrome waste could produce various soluble compounds. Cr^{III} and Cr^{VI} compounds are produced in large quantities and are accessible to most of the population.. Usually, poisoning by Cr^{VI} results in acute tubular necrosis of the kidney, the reported cause of death5. Prolonged contact with certain chromium components may produce allergic reactions and dermatitis in individuals[5]

2 Theory

The problem is concerning the possibility of oxidation of Cr^{III} into Cr^{VI} in gentle conditions by air in the wide range of pH. Principally oxidation can be realized after the following equations:

$2Cr_2\,O_3 + 8OH^- + 3O_2 = 4Cr\,O_4^{--} + 4H_2O$

in alkali medium and

$2Cr_2\,O_3 + 3O_2 + 2H_2O = 2Cr_2\,O_7^{--} + 4H^+$

in acid medium.

The probability of the spontaneous oxidizing process Cr^{III} into Cr^{VI} is real as shown from the Gibbs Energies of both reactions. From published thermodynamics functions - Gibbs Energies of Formation[6]:

Component	**Gibbs Energies of Formation** $\Delta Gf^\circ kJmol^{-1}$
$Cr_2\,O_3$	-1053
OH^-	-157.28
O_2	0
CrO_4^-	-727.85
H_2O	-228.61
$Cr_2O_7^-$	-1301.2
H^+	0

we calculate Gibbs Energy both reactions

$\Delta Gf^\circ =$ -4 x 727.85 – 4 x 228.11 - (2 x 1053 – 8 x 157.280) = - 459 kJ for alkali medium, and

$\Delta Gf^\circ =$-2 x 1301.2 – (2 x 1053 – 2 x 237.14) =

= - 22.12 kJ for acid medium.

The negative values of both thermodynamic functions prove the possibility of spontaneous oxidation within a wide range of pH. We propose the closed loop for recycling chromium not only from solid but also from liquid wastes. The scheme of totally reusing chromium of our proposed process is in the following Figure 1.

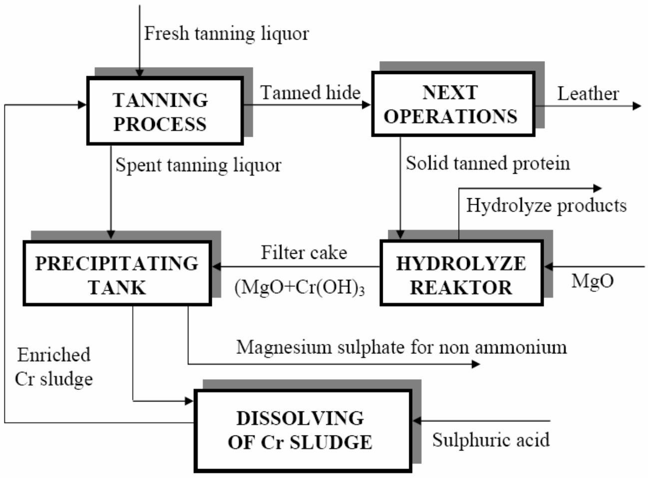

Figure 1. Closed loop for chromium recycling in beam-houses

Model of Chromium Total Recycling Process

To determine optimal time for dechromation of spent liquor, we assume filter cake is in a filter press through which solution of chromium ions circulates. The technological scheme is shown in Figure 2.

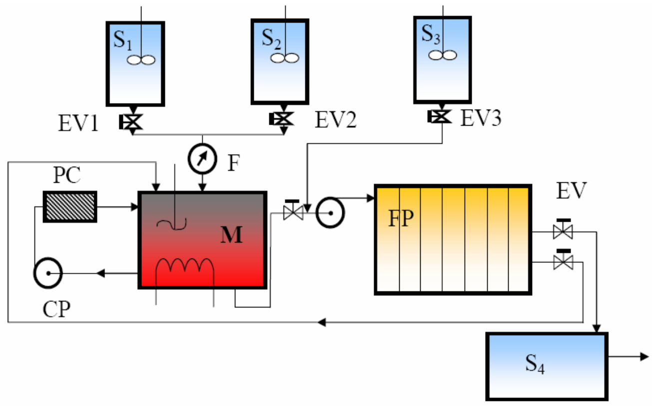

Figure 2. Dechromation of spent liquor

Legend:

F – flow meter, EV – electromagnetic valve, PC – photocell, FP – filter press, CP – centrifugal pump, S_1 – spent liquor storage tank, S_2 – water solution of NaOH or Na2CO3 storage tank, S_3 – filter cake suspension storage tank, S_4 – $MgSO_4$ Na_2SO_4 water solution storage tank

On attaining optimal time, the remaining content of chrome is precipitated with a strong alkali, e.g. sodium carbonate or sodium hydroxide. Chief operating costs N_T are determined by the sum of the costs of power consumed by electric motor of centrifugal pump N_E and the price of consumed alkali N_A.

$$N_T = N_E + N_A \tag{1}$$

The costs of consumed power are determined by a product of unit price K_E, motor input P and time τ during which the centrifugal pump is in operation. The costs of additional precipitation of chromic ions are proportionate to alkali unit price K_A and its consumption n_A.

$$N_T = K_E P\tau + K_A n_A \tag{2}$$

The sum of molls nA depends on the molar concentration of residual chromium c and total the volume of processed spent liquor.

$$N_T = K_E P\tau + K_A V c\beta \tag{3}$$

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

$$2Cr^{+++} + 3Mg(OH)_2 = 2Cr(OH)_3 + 3Mg^{++}$$

In the case transport process (diffusion) is excluded, the rate of precipitation reaction is:

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

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

$$-\frac{dc}{d\tau} = kc^2, \quad where \quad k = k_1 c_n^3 \tag{5}$$

Integration of (5) gives:

$$\frac{1}{c} - \frac{1}{c_p} = k\tau \tag{6}$$

from where

$$c = \frac{c_p}{k\tau c_p + 1} \tag{7}$$

where c_p is the starting concentration of chromic ions in spent liquor. Substituting (7) into (3), we obtain:

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

The following Figures 3, 4 show the dependence of chief operating costs on time with given parameters of spent liquor volume and with value of precipitation reaction rate constant.

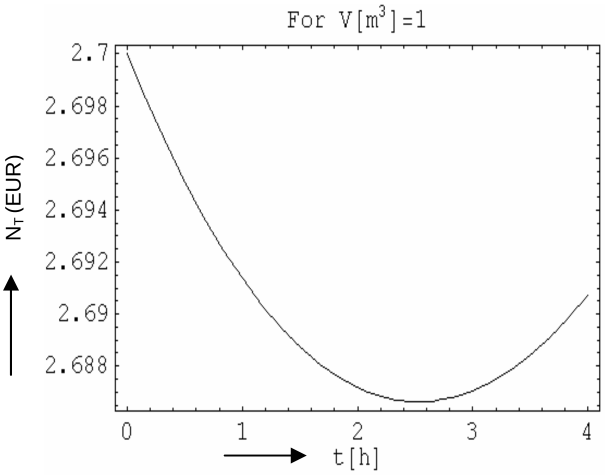

Figure 3. Cost function for V=1m^3

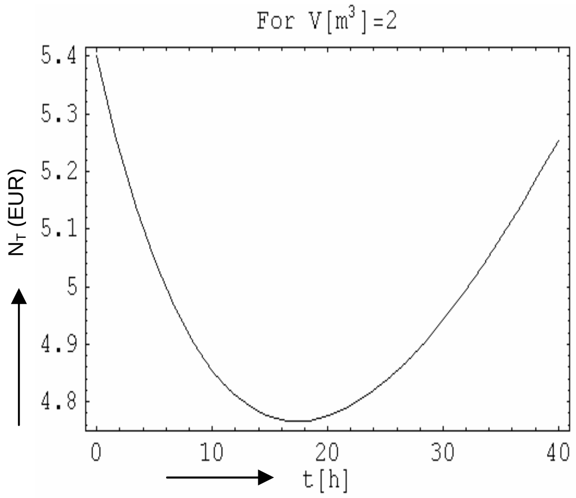

Figure 4. Cost function for V=2m^3

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

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

From that

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

The following Figure 5 exhibits a dependence of optimal time on volume of spent liquor and rate constant of precipitation reaction Figure 6.

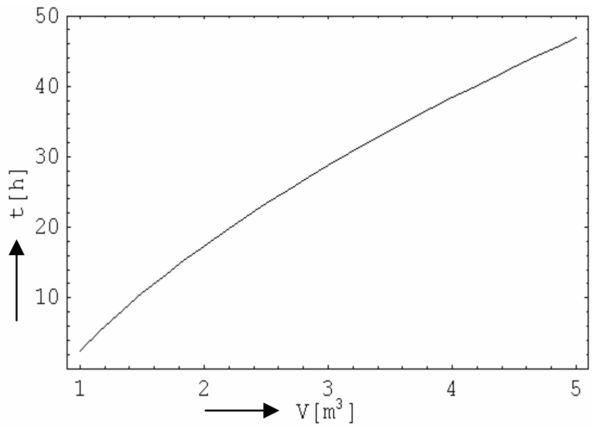

Figure 5. Dependance of optimal time on spent liquor load

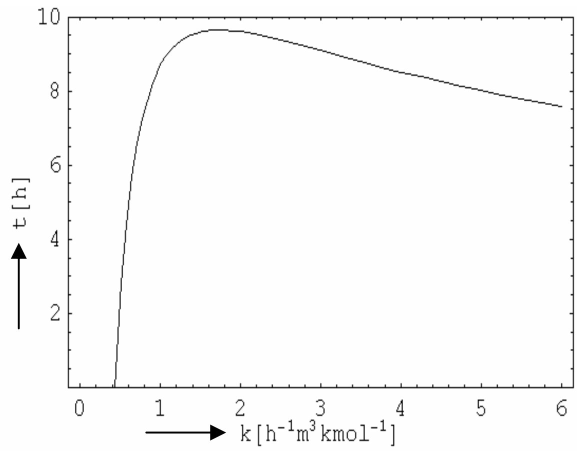

Figure 6. Dependance of optimal time on speed constant

2 Laboratory Model Control System

For the verification of our own technology and measuring and control system, a special laboratory model was built there. The recycling process technological and hardware scheme is shown on Figure 7. For the main part, there are vessels and a measuring storage tank with a mixer and sensors, which are situated in it.

The processed wastes are put into it. This equipment is fitted out with necessary sensors and valves for reading physical quantity and control of action elements.

It is necessary to control and display in the recycling process:

- Filling process liquid and solid wastes with a defined amount.
- Scanning discreet signals defining the position or state individual procedure parts of technological system and taking analogy values from the process.
- Control of the time sequence of an individual operation according to a technological procedure with controlling of all parameters.
- Communication of the control system and server via the serial link RS 232.

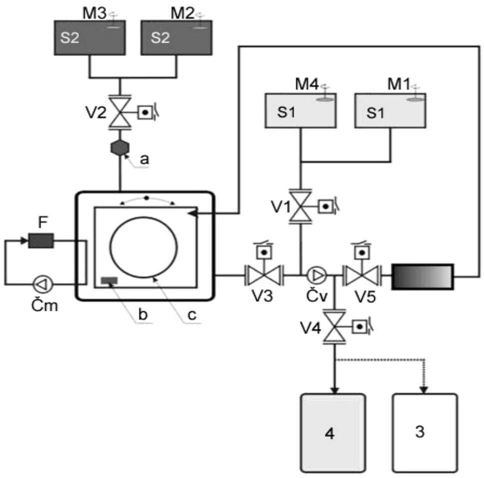

Figure 7. The simplified schema of technological equipments

Legend:
S1 - Vessel with solid wastes Cr^{III}; S2 - Vessel with liquid wastes; Čv,Čm – Centrifugal pumps; V1,V2,V3,V4,V5 – Electromagnetic valves; c – Washer; F - Photosensor of concentration; a - Sensor of flow rate; b - Sensor of temperature; 3, 4 - Vessels with finished products.

Control consists of the commanding of equipments and measuring out of chemicals according to a planned program.Quantitatively higher-level automatic control is the using of a backward connection, when action interference is made on the basis of real parameters of the process, which are just going.

Programming methods in applied in automation application

Described technology is now implemented in laboratory conditions in our department by a computer control system with a programmable industrial card Advantech PCL – 812/812PG, which has its own A/D and D/A converters. Each part of the technology process has its own control subsystem for the direct digital control of the physical values as temperature, water level in the vessel, concentration etc. The software system is built in the C language. For the real time running of the program system there is used a special pre-emptive real time operating system RTMON, which was built for the using of a monitoring and control system for technological processes. It allows multitasking of defined a number of processes. User's programs are structured on the basis of the priority hierarchically. The choosing of the program, which will be running on the processor, is carried out on the basis of its priority level. The structure of an application programs is shown in Figure 8.

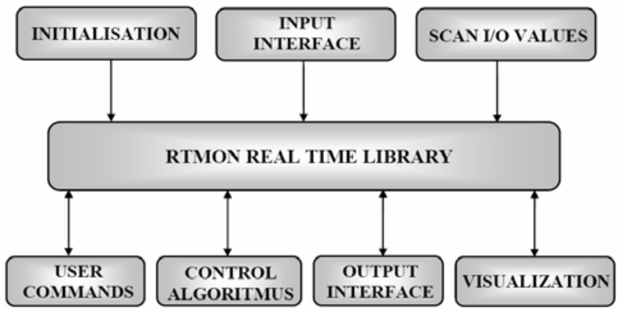

Figure 8. Real time control system

The program system includes the basic part of the real time operating system and is created by process modules[6]. INITIALISATION is a process which defines the data structure of the real time operating system and fills the program variables by the initial values; another process SCAN I/O VALUES reads periodically the binary and analogue input values. The CONTROL ALGORITHMS processes calculate optimal time to filling it into the bath from the measured values of temperatures, value of turbidity and temperature control. The process COMMUNICATION ensures the communication between both levels of the control system via the serial link RS 232. The VISUALISATION process allows us to send and to get back the information and important parameters with DDE server and software Wonderware InTouch. Through the process USER COMMANDS operating staff of technological equipment can operate the technology processing.

Temperature control

For the identification of the controlled system we have generated an inputted unit signal. Reaction of this signal is the step response. The identification was created by means of personal a computer. The program was written in C language. This program archived the measured values, which can follow mass processing by means of another program. For this function was used program the Excel, the part of the Microsoft Office. The thermal system has the following transfer function:

$$G(s) = \frac{1,12}{(4610,1s+1)(375,2s+1)} \tag{11}$$

We designed different controllers for the control. The good results show the controllers with dynamic inversion[9]. For the time period T=700s we have a transfer function of discrete PID controller in the form

$$G_R(z^{-1}) = \frac{2,9505z^{-1} - 2,9916z^{-1} + 0,3924z^{-2}}{1 - z^{-1}} \tag{12}$$

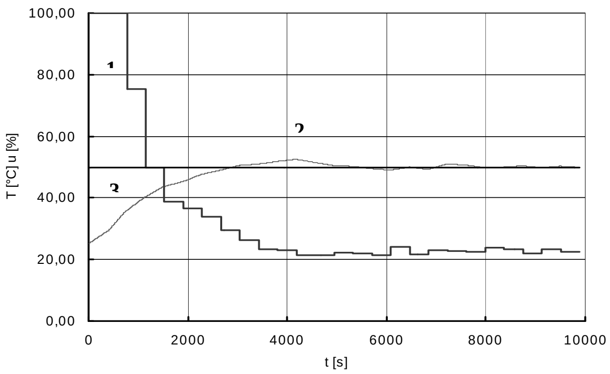

Figure 9. The real measuring. Controllers designed by dynamic inversion[7] (1-controller output, 2-reference value, 3-controlled value)

The temperature control is shown in Figure 9. We can see that the time period to stabilization on the reference value is somewhere around 5000s with no overshooting. These shots are necessary for system parameters determination.

4. Conclusion

In our concise contribution we have proved, as we firmly believe, the successfulness and necessity of indirect modelling for the rationalisation of the leather industry. The mathematical simulation of leather manufacturing processes has not been used yet to the needed extent. The purpose of the methods suggested by us – the use of the theoretical tools of process engineering – has a fundamental importance particularly for the forthcoming important task, namely the elaboration of recycling technologies not only for primary wastes (tanning processes) and the secondary ones (footwear industry), but also for the used products. It is necessary to deal with the problems of concentrated collecting of used-up shoes, and especially the technology of their dechromation. Therefore, the principal question is about chromium-tanned wastes in which, as we have shown, the trivalent chromium is highly unstable from the thermodynamical point of view. From the many publications dealing with the above-mentioned topic let us name at least these two[8,9], which point out the presence of the hexavalent chromium in leather products. It is necessary to focus intensively on this fact and to elaborate such recycling technologies that enable us to have the potentially dangerous chromium under control and to protect human health and lives that way.

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