

# Software for Automatic Control System for Dechromation of Tannery Waste

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**Abstract** - This paper deals with implementation of software system which controls the process of removing chromium from recycling chromium from tannery waste. The laboratory is used to research and improve unique chromium-recycling technology based on enzymatic hydrolysis developed at our institute and the described system is the main control component of a part of the technology. First, the concept of the whole technology is briefly summarized, and then the paper focuses on the control system for dechromation of tannery waste water.

**Keywords:** - tannery waste, Control Web, Chromium, Advantech.

## I INTRODUCTION

Computer-based systems are becoming the standard for controlling technological processes. Especially if the process requires complicated evaluation of several inputs and computation of results based on these inputs, it is hardly possible to control such process without computer and suitable software. One of the areas where such relatively complicated control systems are used is in the modern processes which are necessary to achieve high efficiency and environment-friendliness.

This article focuses on tannery industry which produces huge amount of waste. In tanneries, only about 20 per-cent of raw hide is transformed into the final product; the rest is waste in various forms. [9] Big portion of this waste contains chromium which is still the most-used agent for hide-tanning in the industry. Despite the fact, that one of its variants, hexavalent chromium, is highly toxic and is proved to cause cancer. As the attempts to find a substitute that would give comparable results as to the quality of the product and production costs were not successful so far, it seems unlikely, that in the near future chromium in tanning industry would be replaced. This makes it important to develop methods for dealing with the waste containing chromium.

The best option is to recycle the chromium and return it into the tanning process or use it in other industrial processes. A method for hydrolyzing chromium waste was developed at our institute, which produces relatively expensive protein hydrolyzates and also chromes sludge [1]. But if any new method is to be successfully implemented in industry, it needs to be optimized in the means of investment and operating costs. For this reason the method is realized in small scale in our laboratory. The main problem now is not the technological solution to recycling chromium from the tannery waste, but the economical part of the problem. It is required that the process is as effective as possible to allow its implementation in the tanneries. For this a computer-based control system is required which can process the inputs and control the system in real time.

## II PROBLEM FORMULATION

This section will briefly introduce the whole technology and then focus on the part which deals with removing chromium from waste water controlled by the described system.

The base of the technology is enzymatic hydrolysis, which appears to be the best method for processing chromium-containing tannery waste both from the economic and ecologic point of view. This technology yields protein hydrolyzates that contain virtually no chromium while the dose of expensive enzyme is less than 1% and the filter cake can be recycled. The complete process is in our laboratory divided into four workplaces called: fermentation, filtration, evaporator and dechromation. Fig. 1 shows the principle of the technology. First step is chemical reaction in fermenter – hydrolysis [2]. Product of this reaction is then filtered and the resulting filtrate (valuable protein hydrolyzate) is dried in evaporator.

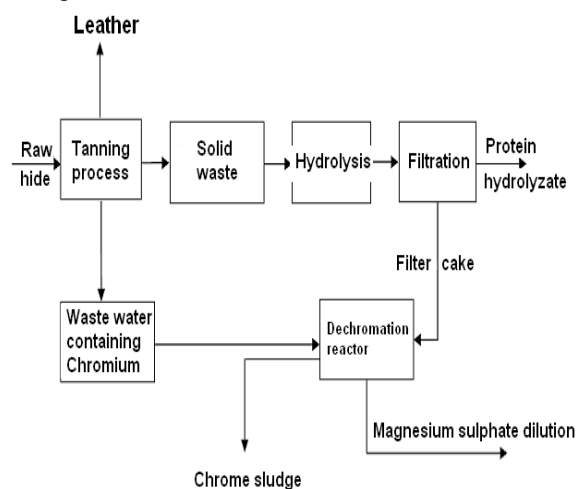


Fig. 1 scheme of the technological process

At the last workplace, the filter cake containing magnesium hydroxide reacts in dechromation reactor with tannery waste water (spent liquor), which needs to be cleared of chromium. The waste water is freed of chromium and the chromium caught in the filter cake can be used in other industrial applications or returned to the tanning process.

This article focuses on the control system for the last workplace, dechromation reactor. The principle of the technology controlled by described system can be seen in Fig. 2. Suspended filter cake obtained at filtration workplace is transported from tank S3 into filter press FP. The tank M is filled with waste water which is then circulated through the filter press by a pump. This circulation continues until concentration of the chromium in this water drops below the level at which further circulation would not be economically

advantageous. After this point it is cheaper to precipitate the residual chromium using alkali.

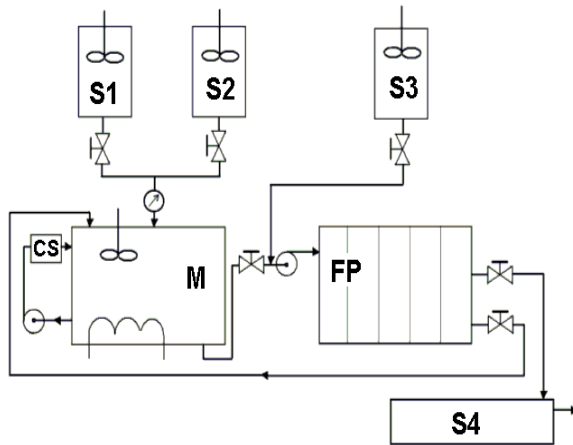


Fig. 2 principle of the technology for dechromation

The necessary amount of alkali is then measured from tank S2 into M and the process is ended.

The task of the control system for this technology can be defined as continuously monitoring the concentration of the chromium in the waste water circulating through the filter press and computing the time required to reach the point, where it is cheaper to stop the circulation and remove the remaining chromium with alkali. This computation is based on equations published in [1]. The total cost of the dechromation is:

$$N_T = N_E + N_A$$

Where  $N_E$  is the cost of running the pump for circulating the water through the filter press and  $N_A$  is the price of the alkali which can be used to precipitate the chromium from the waste water.

The price for running the pump can be defined as:

$$N_E = K_e P t \quad (2)$$

where  $K_e$  is the unit price of of electric energy,  $P$  is the input power of the pump and  $t$  is the time the pump is running.

The price of the alkali  $N_A$  is:

$$N_A = K_A \cdot n_A \quad (3)$$

where  $K_A$  is unit price of the alkali and  $n_A$  is needed number of units of the alkali.

The needed amount of alkali can be expressed as follows:

$$n_A = V \cdot c \cdot \beta \quad (4)$$

where  $V$  is the volume of the waste water,  $c$  is the concentration of chromium in the water and  $\beta$  is stoichiometric coefficient of the precipitating reaction which takes place in the filter press.

By substituting the above relations into (1) we obtain:

$$N_T = K_e P t + K_A V c \beta \quad (5)$$

The rate of the precipitation reaction in the filter press is:

$$-\frac{dc}{dt} = k_1 c_n^3 c^2 \quad (6)$$

where  $c_n$  is concentration of magnesium hydroxide in the filter cake. Provided we use excess concentration of magnesium hydroxide in the filter cake, it can be considered constant and the equation 6 is simplified to:

$$-\frac{dc}{dt} = kc^2 \quad (7)$$

where:

$$k = k_1 c_n^3 \quad (8)$$

After integration of (7) we obtain:

$$\frac{1}{c} - \frac{1}{c_p} = kt \quad (9)$$

From this we can see that the concentration of chromium is:

$$c = \frac{c_p}{kct_p + 1} \quad (10)$$

(1) where  $c_p$  is the starting concentration of chromium in the waste water.

After substituting (10) into (5) we obtain the following equation for the total cost of dechromation:

$$N_T = K_e P t + \frac{c_p K_A V \beta}{k \cdot c_p \cdot t + 1} \quad (11)$$

The optimal time for dechromation can then be obtained by differentiating this equation with respect to time:

$$\frac{dN_T}{dt} = K_e P - \frac{c_p^2 k K_A V \beta}{(kc_p t + 1)^2} = 0 \quad (12)$$

The resulting optimal time for circulating the water through filter press is:

$$t_{opt} = \sqrt{\frac{V \beta K_A}{K_e P k}} - \frac{1}{kc_p} \quad (13)$$

Where  $V$  is the volume of the water circulating through the filter press,  $\beta$  is stoichiometric coefficient of the reaction (which is 3 in this case),  $K_A$  is the price for unit amount of alkali,  $K_e$  is the price for running the pump for 1 second,  $k$  is the speed constant of the reaction of the chromium in the waste water with the magnesium hydroxide contained in the filter press and  $c_p$  is the starting concentration of chromium in the water.

As can be seen from the (13) we replaced the price for unit of energy  $K_E$  and input power of the pump  $P$  by price for running the pump for a unit of time  $K_P$ . This is because the pump in our system is not powered by electricity as expected by the original equations but by compressed air. By making the  $K_P$  one of the inputs of the program we obtain more versatile solution which allows the user to define the price for running the pump without assuming anything about the kind of power etc. In our case the compressed air is taken from central pipeline in the building and determining the price for running the pump is not trivial. Because of this in the experiment we estimated the price based on the price for running electrically powered pump of equivalent performance.

As already mentioned the control system continuously measures concentration of chromium in the waste water and computes the optimal time  $t_{opt}$  according to (13). When the time of circulation already exceeded the computed optimum time, the system stops the cycle.

### III CONTROL SYSTEM

This section describes the control system developed for controlling the dechromation reaction. The description is divided into 2 main chapters, hardware and software, with focus on the software implementation. The hardware of the system has been described in more details in [4].

#### A Hardware of the control system

The control system for the dechromation workplace is depicted in Fig. 3.

The central part of the control system is industrial panel PC Advantech PPC-L126T-R70 with 12" touch screen and Windows XP operating system. It allows comfortable control and visualization of the technology directly at the workplace. The computer is equipped with Via processor running at 667 MHz with low power consumption and passive cooling which allows maintenance free operation for long time. To connect the computer to the technology, we used Advantech ADAM modules. These modules are connected via RS 485 bus which is connected to the RS323 port of the panel PC through RS 232/485 converter ADAM 4520. To connect the computer to the technology, we used Advantech ADAM modules. These modules are connected via RS 485 bus which is connected to the RS323 port of the panel PC through RS 232/485 converter ADAM 4520.

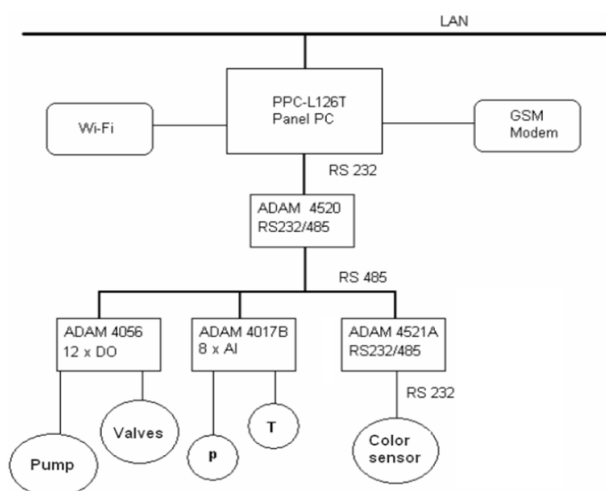


Fig. 3 scheme of the components of the control system for dechromation workplace

The following ADAM modules are used:

Digital output module ADAM 4056S – to control the actuators (solenoid valves and pump). The module provides 12 outputs with open collector only, so there is a converter (relay) box between the module and the actuators.

Analog-input module ADAM 4017B – used for sensors with current or voltage output.

For measuring temperature in the tank and pressure in the filter press sensors with current outputs (4 to 20 mA) are used. The concentration of the chromium in the water is measured by color sensor HDSC16 which communicates with the computer via serial line and reports the color as RGB values [3]. The waste water is circulated through this sensor using small pump as can be seen in Fig. 2. This pump is powered by 24V controlled by one of the digital outputs from ADAM 4056S.

#### Converter box

There is a converter box between the actuators and sensors and the ADAM I/O modules connected to the computer, which was created mainly to allow controlling the solenoid valves with 230V input by the ADAM I/O modules with open collectors.

The converter box provides the following functions:

- Computer control of the solenoid valves operating at 230 Volts AC.
- Computer control of two heating elements in the tank M (230V AC). These are controlled by solid state relays to enable PWM modulation of the power.
- Computer control of pneumatic valves operating with 24V DC.
- Computer control of the pump for color sensor (24V DC)
- Power for all the above elements from a single 230V AC supply.

The converter box contains three PCB boards: board for 230V relays and solid state relays, box for 24V and 12V relays and 12V power supply board.



Fig 4 control board with panel PC, ADAM modules and converter box.

It also contains 24V/3A power supply for the pneumatically operated valves and for the color sensor. Both the relay boards are interfaced using 25-pin Canon connector located at the upper side of the box. The inputs and outputs from ADAM I/O modules are connected to this connector. Power wires are connected to terminal blocks and they exit the box on the left side.

### Color sensor

The sensor which measures the concentration of chromium in the waste water is important part of the system. In this place a colorimetric sensor is used. Various options for sensing the color change can be used, for example it is popular to use a web camera and obtain the result by processing the image from this camera in special software. We decided to use a dedicated color detector HSCD16 made by m.u.t. GmbH Company based in Germany. HSCD16 is a high speed detector system for precise color detection in fast sorting processes. Up to 16 colors can be pre-set with a build in "Teach mode". The HSCD16 is based on RGB-color detection. The detection process can be started with a trigger signal or via the build in RS232 interface from any external device. The detection process and/or the "good/bad" evaluation is extraordinary fast and precise. The manufacturer suggest wide range of possible applications for the HSCD16 sensor in many industries e.g. sorting of blood sample tubes in clinical laboratories, any sorting or separation processes based on color detection such as manufacturing, quality assurance etc. The main features of the detector are:

- Wavelength range 400 to 750 nm
- Focus (distance from housing) 17,2 mm
- Intensity 1,4 mW (at 400 nm)
- Maximum 880 color measurements per second
- RS 232 interface
- Power supply 8 - 30V (typ. 24V), 4 W

The sensor can be seen in the scheme of the technology as "CS" in Fig. 2. It is connected to a pipe on a side of the tank M and the liquid is circulated through the sensor with a small pump, measuring the color of the liquid continuously.

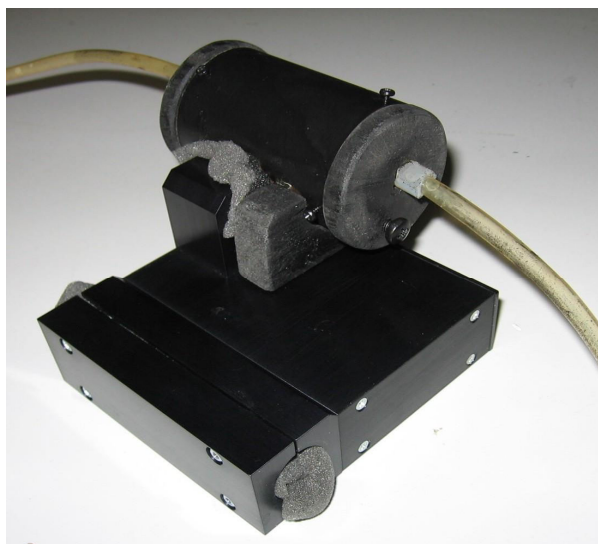


Fig. 5 color sensor with the adapter attached

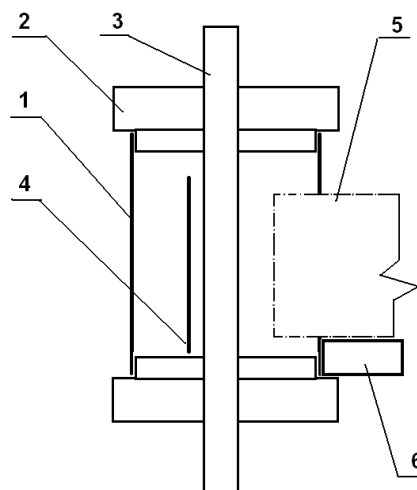


Fig. 6 scheme of the adapter for color sensor

However, because the sensor is manufactured for different kind of operation an adapter was needed to make the liquid flow in the focus of the sensor. The adapter also shields the measuring environment from ambient light so that the results do not depend on the light conditions of the room. The sensor has its own light source.

The adapter we have constructed can be seen in Fig. 6. The core of the adapter is a glass pipe 3, which makes the liquid flow in the focus of the sensor. The frame of the adapter consists of plastic tube 1 and two lids 2. There is a slit in the tube which allows it to be attached and fixed to the body of the detector 5 and a special part 6 which defines the position of the adapter on the sensor body, so that the focus is properly adjusted. Also there is a small mirror 4 from aluminum plate which proved to be necessary for the sensor to work properly.

### B Software of the control system

The user interface of the software consists of full-screen window with tab selector on the right side, see Fig. 7. The user can choose the appropriate tab according to the operation he/she intends to perform. There are tabs for manual control of the workplace, for semi-automatic and automatic control and for archiving the process. When selected, the tab displays its content in the left part of the window.

Besides the tab selector there is also information about the current temperature, pressure and water color displayed all the time, for all tabs. There is also central stop button for emergency shut down of the actuators.

In Control Web applications, most of the code in is bound to graphical components on the screen (so called virtual instruments) and the following description of the system is therefore organized according to the tabs and their virtual instruments.

#### Manual control tab

This tab provides GUI for controlling the technology on the level of individual elements, such as solenoid valves.

The scheme of the workplace is shown on the screen and the user can simply control the elements by touching the screen.



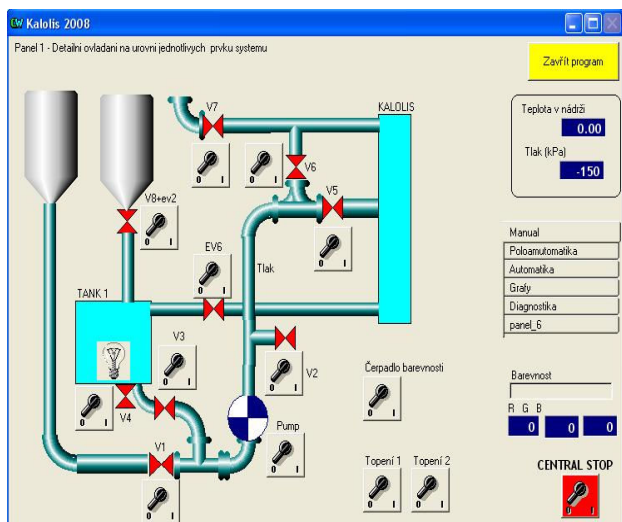


Fig. 7 control program – manual control tab

The controls in this tab are Control Web “switch” instruments which have their “output” property set to the appropriate channel of ADAM 4000 driver.

### Semi-auto control tab

In this tab the user can select a phase of the technological process, e.g. filling the filter press, and start this phase by single command instead of manually switching the required valves one by one. The main control in this tab is a combo box containing available phases.

User selects a phase and then starts it by the switch. The implementation is as follows: when user activates the switch, its procedure OnOutput detects the selected item in the combo box and calls custom procedure “ActivateAction” which sets the outputs according to given action code. The interaction with the ADAM I/O modules is performed through a “program” instrument named “programAdvantechIO”, which serves as an interface between various parts of the program and the actuators.

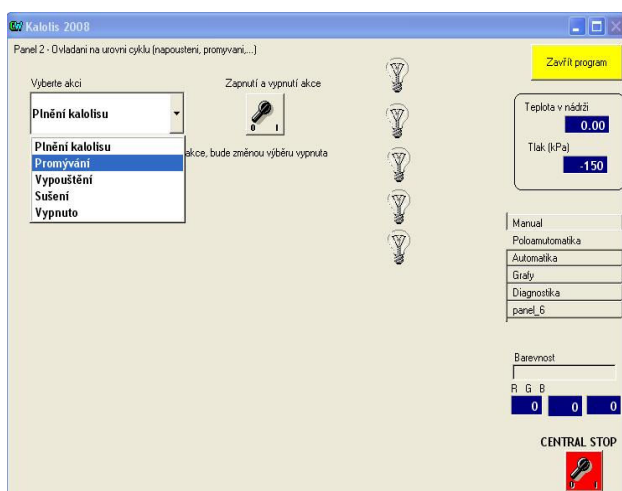


Fig. 8 control program – semi-automatic control tab

### Automatic control tab

This tab is used to control automatic dechromation of the waste water. The user enters the input parameters and then can start the dechromation. The input parameters include: volume of the waste water, price for 1 second of pump operation, price for 1 g of alkali and required concentration

of the chromium at the end of the cycle. Once the dechromation is started it will be automatically ended when one of two conditions is met: either if the operation is already running longer than the optimal time, or if required concentration of the chromium is reached. The process can also be stopped at any time by the user. During dechromation, this tab displays the time from the start, optimum dechromation time as currently computed, chromium concentration etc.

The implementation for this tab is based on “selector” instrument which allows branching of the execution according to logical expressions. Each branch has a name and if the condition of this branch is met, all instruments which have this branch name set as their “timer” parameter are activated. In our program these activated instruments are “program” instruments, each of which handles one phase of the process such as calibrating the color sensor, circulating the water or error handler. In the programs it is also ensured that once the execution reaches its end, it changes a state variable to activate the next program by the selector.

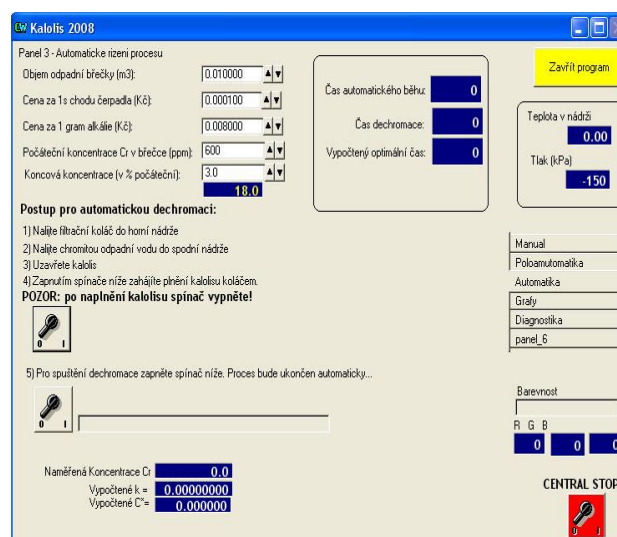


Fig. 9 control program – automatic control tab

### Graphs and archive tab

This window (see Fig. 10) allows the user to view the charts of the measured values – temperature in the tank, pressure in the filter press and the color of the waste water (R, G and B values). It is also possible to control the archive feature for these values.

The application allows storing measured values into database. This utilizes the Archive section feature in Control Web, which stores selected variables with given time-period into MS Access database file. In our application there are two sections (and thus two database tables) used. First is for archiving the measured values and the second logs the results of computations for the automatic control of the process.

### Diagnostics tab

The application contains also diagnostics tab which contains information useful for debugging the program and solving problems with the system. This tab allows, for example, controlling the color sensor using text commands and displaying the response from the sensor. This tab is

intended for advanced users and system developers only and in the final application it will be hidden or blocked.

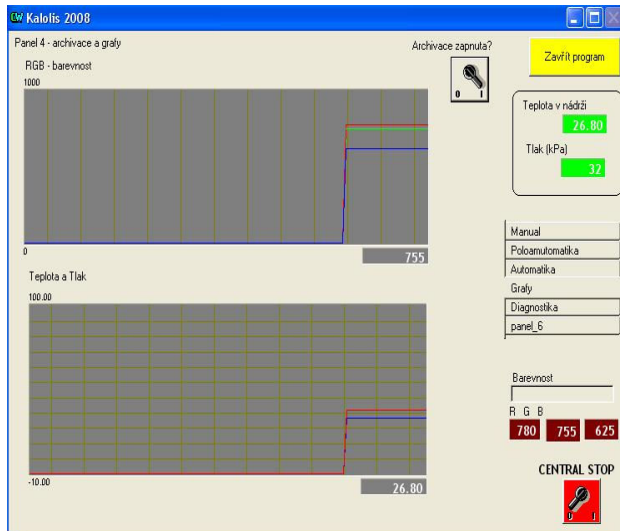


Fig. 10 control program – graphs and archive tab

### Verification of the system

For the verification of the system it was first necessary to determine the dependency of the output of the color sensor (RGB values) on the concentration of chromium in waste water and then an experimental dechromation was performed.

Table 1 Output of the color sensor for water solutions with known concentration of chromium

Chromium concentration [ppm]	Output of the color sensor		
	R	G	B
625	502	313	343
313	716	579	563
208	805	710	656
156	854	788	707
125	880	830	734
104	898	862	754
69	937	927	775
57	950	948	809
39	966	972	824
30	977	984	838
24	976	983	847
15	976	983	865
12	976	983	866
8	976	982	871
0	975	982	898

### Dependency of the chromium concentration on the waste water color

The relationship between water color and concentration of chromium in this water had to be determined first. This was done using several samples of water with known concentration of chromium. The measured output values of the sensor for given samples with known chromium

concentration can be seen in table 1. Chart of the dependency is depicted in Fig. 11.

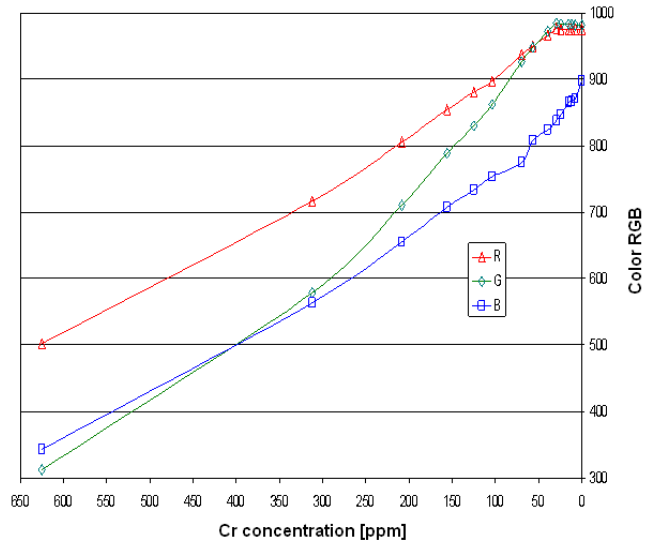


Fig. 11 chart of the dependency of RGB values on concentration of chromium

For computing the chromium concentration from the measured RGB values we determined the analytical dependency. The concentration of chromium  $c$  is a function of the R, G and B values (the red, green and blue components of the color):

$$c = f(\text{color of the water}) = f(R, G, B) \quad (14)$$

The dependency for each color component is:

$$c_R = f_R(R); \quad c_G = f_G(G); \quad c_B = f_B(B) \quad (15)$$

These dependencies were approximated by logarithmical functions as follows:

$$c_R = -919,15 \ln(R) + 6350.1 \quad (16)$$

$$c_G = -533,02 \ln(G) + 3698.5$$

$$c_B = -668,62 \ln(B) + 4535.2$$

In the Fig. 12 the comparison of the approximated and measured values can be seen.

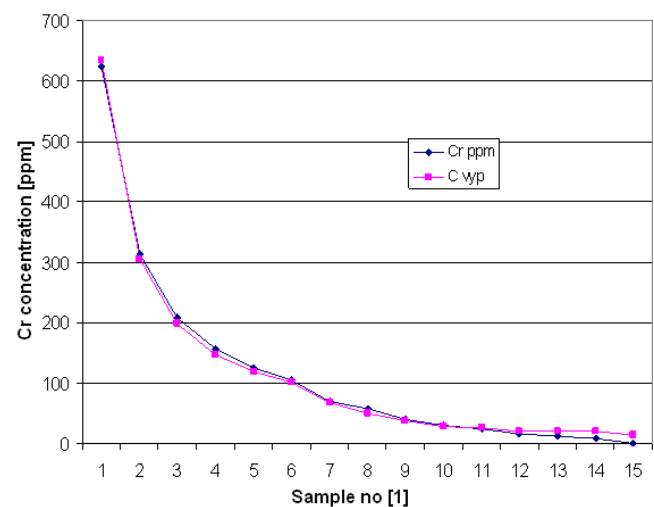


Fig. 12 comparison of measured and computed concentration

### Experimental dechromation

In the second part of the verification an experiment was performed in which a filter cake was prepared and then used in the filter press to clear waste water of chromium. The measured values were recorded and later used to compute the optimum time and verify the results of the program.

The input was 1.8 kg of filter cake with 13.8% dry mass and waste water containing 625 ppm of chromium. The chromium concentration was determined using atomic absorption. In the course of the experiment the filter cake was first diluted by 5 liters of water so that it could be filled into the filter press. In the control program the appropriate valves were opened to fill the filter cake. During filling about 5 liters of water accumulated in the tank. This water was removed and then the tank was filled with 10 liters of waste water containing chromium. The pump for the color sensor was turned on, the appropriate valves were opened and the pump for circulating the water through the filter press was turned on.

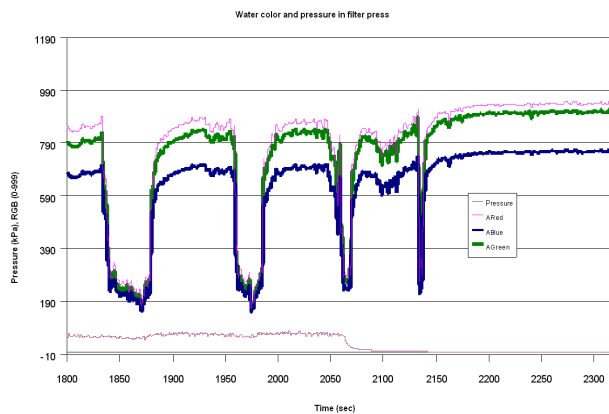


Fig. 13 Results of experimental dechromation

During the circulation the measured data were recorded into database. The program proved to be working correctly. Fig. 13 shows the record of change of the color of the water (RGB values) and pressure in the filter press. In the figure the RGB values are depicted as they change in time. There can be seen sudden drops in these values which were caused by refilling the tank with the water leaked from the filter press during the circulation. This water was caught into a bin and then put back into the tank which caused turbulence and disturbed the color sensor reading. This leads to a recommendation to arrange the system so that the leaked water is continuously brought back into the tank or to use a big enough bin to catch the water and put it into the tank only after the end of the dechromation (to be processed in the next cycle).

### Verification of the results

From the values recorded during the experiment we selected six points in which the chromium concentration was computed to verify the method, see table 2.

Table 2 Change of  $C_t$  concentration during the experiment

Run time [sec]	0	450	620	720	1020	1100
Conc. of Cr [ppm]	625	156	150	140	80	70

For each of the points the computation described below was carried out. Here is an example for the time 450 s.

First,  $C^*$  is computed:

$$C^* = \frac{c_p - c}{c_p c} \quad (16)$$

where  $c_p$  is the starting concentration of Cr, here 625 ppm.

Substituting the real values we obtain:

$$C^* = \frac{625 - 156}{625 \cdot 156} = 0,00481 \quad (17)$$

The dependency of  $C^*$  on time is in ideal case linear and the tangent of this line is the speed constant of the chemical reaction which removes chromium from the waste water (see (9) and (10) above).

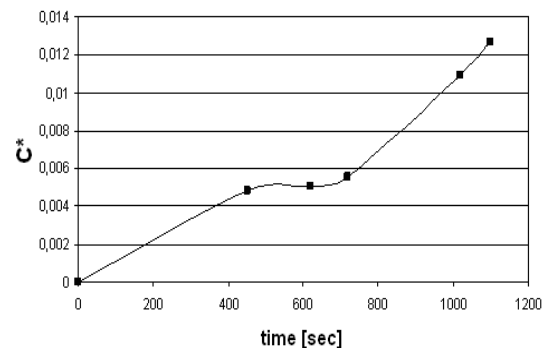


Fig. 14 dependency of  $C^*$  on time during the experiment

The dependency of  $C^*$  on time can be seen in picture 14. However, the program can only use the values measured up to the current time when it computes the optimum time during the dechromation. Therefore it computes the speed constant  $k$  as follows:

$$k = \frac{C^*}{t} \quad (18)$$

For the time 450 s we obtain:

$$k = 1,069 \cdot 10^{-5} \quad (19)$$

The optimal time of dechromation can then be computed as follows (see (13) above):

$$t_{opt} = \sqrt{\frac{V\beta K_A}{K_p k}} - \frac{1}{kc_p} = \sqrt{\frac{0,01 \cdot 3 \cdot 0,01}{6,94 \cdot 10^{-5} \cdot 1,07 \cdot 10^{-5}}} - \frac{1}{1,07 \cdot 10^{-5} \cdot 625} = 487 \text{ s} \quad (20)$$

The input parameters were as follows:

- Volume of the waste water:  $V = 0,01 \text{ m}^3$ .
- Price of the alkali:  $K_A = 0.01 \text{ CZK/gram}$
- Price for running the pump:  $K_p = 6.944 \cdot 10^{-5} \text{ CZK/s}$
- Starting concentration of Cr:  $c_p = 625 \text{ ppm}$

- Stoichiometric coefficient of the reaction:  $\beta = 3$
- For time 450 seconds we thus obtain  $t_{opt} = 487$  s

This means that after 450 seconds the program will not yet stop the circulation of the waste water through the filter press because the computed optimal time is longer than the current time of run. Table 3 summarizes the results for the selected time points.

Table 3 Summary of the results

čas [s]	c	C*	k	$t_{opt}$
0	625	N/A	N/A	N/A
450	156	0,00481	1,07E-5	487
620	150	0,00507	8,17E-6	531
720	140	0,00554	7,70E-6	541
1020	80	0,0109	1,07E-5	486

As can be seen in the table, the experiment ran longer than it is economically advantageous; in time 620s the computed optimal time was already shorter than the running time and the automatic control system would end the dechromation. In Fig. 15 the dechromation workplace can be seen. The blue filter-press is in the front, the control board with converter box, ADAM modules and panel PC can be seen in the background.



Fig. 15 The dechromation workplace

#### IV CONCLUSION

Increasing emphasis on environment friendliness and rising prices of materials and energy call for cutting down the production costs and better handling of waste in the tannery industry. One of the methods which allow efficient solution for tannery waste is method based on enzymatic hydrolysis. This method is advantageous in the fact that it handles liquid and solid waste at the same time and also produces high-quality protein which can be used in the industry and also chromium, which can be returned to the tannery process or used elsewhere in the industry.

This paper describes the software system for automatic control of the process of removing chromium from tannery waste-waters. The complete process of recycling chromium from both solid and liquid tannery waste is realized in laboratory scale at our institute and it consists of four workplaces.

The paper focuses on one of these workplaces, where the liquid waste from tannery process is freed of chromium.

The beginning of the paper briefly describes the hardware of this workplace and then it concentrates on the software system which allows automatic dechromation of waste water. The control system is implemented in Control Web development environment and running on the panel PC with Windows XP operating system which is used on the workplace. It consists of several windows selected by tab selector, which the user can control by touching the screen of the control computer. The software allows three modes of operation of the workplace: manual, with individual control of each element (e.g. solenoid valve); semi automatic mode with control of the phases of the technological process (e.g. filling the filter press); and automatic mode where the user only enters initial values and the system continuously measures process values and automatically decides when the dechromation should be stopped. It also allows archiving measured and computed values into database and viewing the charts of the values in real time.

The results of experimental verification of the system compose the last part of the paper. Data obtained during experiments with the system are presented as well as the example computations and their results.

#### ACKNOWLEDGMENT

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