

# Mathematical model of extraction decelerated by diffusion on particular case in leather waste processing

M. Bařinová and K. Kolomazník

**Abstract**—Leather manufacturing processes generate considerable amount of both solid and liquid waste. Especially chromium shavings represent potentially hazardous waste the processing of which is desirable not only from the economic, but particularly from the environmental point of view. To achieve the required quality of the resulting products it is crucial to remove some of the chemicals used during the treatment. The most important compound from this aspect is magnesium oxide (MgO). The most perspective method so far – extraction with diluted sulfuric acid – does not lead to total removal of MgO from the chromium cake. The contribution deals with the modeling of MgO extraction from chromium cake obtained by the filtration after alkaline hydrolysis of chromium shavings. We have studied in detail the conditions that could affect this technological procedure. The mechanism of the MgO extraction was studied through potentiometric titration and the kinetics data of the reaction of MgO with sulfuric acid within the given range of pH were obtained. Based on the experimental data, a mathematical model was proposed describing the extraction of MgO from chromium cake. The model will be further used as a tool for optimization of the extraction process.

**Keywords**—Alkaline hydrolysis, chrome-tanned waste, diffusion, magnesium oxide, mathematical modeling, titration,.

## I. INTRODUCTION

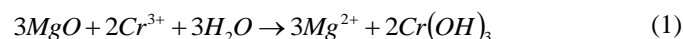
CONVERSION of raw hides into leather is a complex procedure that involves a series of operations (liming, tanning, etc.) connected with addition of components necessary for appropriate technological performance (water, electric power, chemicals). The entire manufacturing process leads to the production of large quantities of waste. Generally, waste generated by leather industry is of two types; non-tanned, generated before the tanning takes place, and tanned, generated during further processing of hides after tanning. Typical and far most abundant representative of the latter are chromium shavings, generated during shaving, an operation

carried out to level out the thickness of the skin and to bring the material to a precise figure. Approximately 80 % of global leather production is tanned with salts of trivalent chromium (Cr III). Chromium III itself is not toxic, but acid rains and other extrinsic factors may lead to its oxidation into hexavalent form (Cr VI) [1], the compounds of which are highly toxic and reported carcinogens [2]. Therefore chrome-tanned waste is classified as hazardous and its disposal in landfills is disputable not only from environmental, but mainly from health protection point of view.

There are various possibilities of environmentally favorable ways of dealing with chrome-tanned wastes, but relatively few have been transferred into industrial practice. The most successful technologies so far are based on two-step alkaline-enzymatic hydrolysis, which is beneficial from both economic and environmental point of view [3]. Detailed description of the hydrolytic process including its industrial applications and automatic control can be found in e.g. [4, 5, 6]. The procedure gives quality products that can be further processed for applications in various industries. Concentrated and isolated chromium can be chemically processed and return to the tanning process, or act as additive for the preparation of industrial pigments [4]. The protein fraction, practically free of chromium, finds application as animal feed or fertilizers of cultivated crops.

To achieve the required quality of the resulting products it is crucial to remove some of the chemicals used during hydrolysis. The most important compound from this aspect is magnesium oxide (MgO), which acts as promoter of the alkaline part of two-step alkaline-enzymatic hydrolysis.

The principle of magnesium oxide removal is based on great difference of the solubility products of chromium and magnesium hydroxides. Chromium hydroxide is practically insoluble in mildly acid conditions (pH ranging from 4.5 to 6); on the other hand, practically total quantitative dissolving of magnesium hydroxide occurs, which is shown in the following reaction scheme [7]:



There are not many reports in the literature on the extraction of magnesium oxide from chromium cake, in spite of the fact that magnesium recycling plays an important role from the

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viewpoint of further processing of alkaline hydrolysis products obtained from chrome-tanned leather waste. An example can be regeneration of chromium by oxidation to its hexavalent form (sodium chromate) in alkaline conditions. The oxidation takes place in furnaces at 800 °C. Serious technological problem in the process represents the presence of magnesium oxide in the filtration cake since it reacts at high temperatures with chromium oxide resulting in the formation of stable corundum [3]. Extraction of magnesium oxide is advantageous also from the economic point of view, since regenerated magnesium can be returned back to the hydrolytic process.

The authors of [7] were measuring the kinetics of dechromation of the waste chromium solution using chromium sludge with a content of MgO. The results showed that it was possible to achieve more than 90% efficiency of the enrichment of the chromium sludge by chromium at the expense of MgO removal. The enriched chromium sludge can be further used for the preparation of green pigments.

Separation of MgO from chromium sludge by 3-stage washing with water is described in [8]. Chromium sludge was mixed with fresh water in various ratios and washing times. The pH of the mixture was kept constant by addition of 10% solution of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). The efficiency of MgO separation reached up to 84 % and the resulting chromium sludge can be used as promising secondary raw material in pigment production.

Based on the above cited paper and a few others (for example [7]), the most efficient methods so far of MgO removal are based on extraction with diluted sulfuric acid. The efficiency of the operation ranges from 80 to 90 %. The fact that the extraction is not complete implies occurrence of either competitive reactions, formation of undesirable intermediate products, or/and influence of other mechanisms such as transport phenomena. Other explanation could be buffering effect of the protein fraction present in the chromium sludge. This possibility has been indicated in [9].

The aim of our contribution was preparation of chromium filtration cake by alkaline-enzymatic hydrolysis and subsequent kinetic measurements of MgO extraction with diluted H<sub>2</sub>SO<sub>4</sub> to determine the reaction mechanism and conditions and propose suitable mathematical model for optimization of the process.

## II. THEORY

### A. Kinetic model of the reaction of MgO with H<sub>2</sub>SO<sub>4</sub>

Let us assume that the reaction of MgO with H<sub>2</sub>SO<sub>4</sub> follows kinetic principles according to the mathematical model presented below. To determinate the velocity constants, we monitored the time during which the pH of the reaction mixture raised from the value of 4.5 to 5 after addition of sulfuric acid (see "Experimental"). Should the reaction actually run in accordance with kinetic principle, the velocity constants in all measurements will not significantly differ from each other. General equation is as follows:

$$\frac{dc}{d\tau} = k(c_0 - c) \quad (2)$$

Since we monitored not the change in concentration, but pH, (1) was adapted to:

$$\frac{dpH}{d\tau} = k[pH_R - pH(\tau)] \quad (3)$$

$$\int_{pH1}^{pH2} \frac{dpH}{pH_R - pH(\tau)} = \int_0^{\tau} k \cdot d\tau \quad (4)$$

After processing and integration of (3) we get:

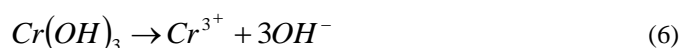
$$k = \frac{\ln \frac{pH_R - pH1}{pH_R - pH2}}{\tau} \quad (5)$$

Where  $k$  stands for the velocity constant [s<sup>-1</sup>],  $pH_R$  is the equilibrium pH (see "Experimental"),  $pH1$  is the initial pH of 4.5,  $pH2$  is the end pH of 5 and  $\tau$  stands for time [s].

### B. Dependence chromium solubility on pH

During removal of MgO from chromium sludge with sulfuric acid we have to take into account not only the range of pH in which the reaction of MgO with H<sub>2</sub>SO<sub>4</sub> takes place, but it is also necessary to monitor the pH range in which chromium oxide dissolves in the acid. Since the aim is to keep the chromium content in the sludge as high as possible, possible dissolving of chromium during the extraction is highly undesirable. As already said above, the pH range in which chromium hydroxide stays stable while practically all magnesium hydroxide is dissolved is from 4 to 6 [7]. However, for practical purposes it is advantageous to identify this range as precisely as possible.

The calculations of the amount of chromium that dissolves at certain pH levels were based on the solubility product  $K_S$  of chromium hydroxide. First it was necessary to determinate the chromium ion content in the filtration cake (chromium sludge). The content (concentration) of Cr<sup>3+</sup> ions in the sludge was related to 50 g of filtration cake. From the mass balance given in Table I in the chapter below, chromium content in filtration cake is 4.88 %, then the weight ratio  $w$  is 0.0488, and dry matter content of chromium cake is 18.42 %, *i.e.*  $w = 0.1842$ . Molar mass  $M_{Cr} = 52 \text{ g} \cdot \text{mol}^{-1}$ . Chromium ions content in 50 g of filtration cake is then  $50 \text{ g} \cdot 0.1842 \cdot 0.0488 = 0.45 \text{ g Cr}^{3+}$ . Dividing the content by molar mass, the amount of substance of Cr<sup>3+</sup> is  $8.65 \cdot 10^{-3} \text{ mol}$ . The solubility product  $K_S$  for chromium hydroxide Cr(OH)<sub>3</sub> is  $6.3 \cdot 10^{-31}$ . Concentration of dissolved chromium ions in the filtration cake dependent on pH level can be then calculated according to the following reaction scheme (6) and equation (7):



$$K_s = [Cr^{3+}] \cdot [OH^-]^3 \Rightarrow [Cr^{3+}] = \frac{K_s}{[OH^-]^3} \quad (7)$$

Below is model calculation for  $pH = 1$ . From the relation for  $pH$  (8)

$$pOH + pH = 14 \quad (8),$$

the concentration of hydroxide ions is  $10^{-13} \text{ mol}\cdot\text{l}^{-1}$ . From (7) it can be then easily calculated that the amount of  $Cr^{3+}$  ions dissolved at the given  $pH$  is  $6.3 \cdot 10^8 \text{ mol}\cdot\text{l}^{-1}$ . When we relate this figure to the amount of substance of  $Cr$  in 50 g of chromium cake, then the amount of substance of chromium ions dissolved at  $pH = 1$  in 50 g of chromium cake is  $31.5 \cdot 10^6 \text{ mol}$ , *i.e.* all the chromium present in the chromium cake. Analogously, the amount of dissolved chromium was calculated for other  $pH$  levels.

### III. EXPERIMENTAL

#### A. Preparation of the chromium cake via alkaline-enzymatic hydrolysis

Two step alkaline-enzymatic hydrolysis was used according to [3]. A total of 3 kg of chrome-tanned shavings and 17 liters of waster were added into laboratory reactor (designed on a washing machine principle) equipped with thermostat. 90 g  $MgO$  (prepared by mashing in a small amount of water) and 60 g  $Na_2CO_3$  were added into the reaction mixture.  $pH$  before heating was around 11. The mixture was subsequently heated to  $70^\circ\text{C}$ . Due to constant reduction of  $pH$  during heating, the  $pH$  was adjusted by repeated adding of  $Na_2CO_3$ , 160 g in total. After that, the  $pH$  remained at the required value of 9-10 and the enzyme (100 ml of 1 % alcalase) could be added. The reaction was terminated after 6 hours from the start of the experiment. The content of the reactor was filtered through dense cloth. The total weight of filtration cake (chromium sludge) was 7 013 g and of filtrate (protein hydrolysate) 10 300 ml. The results of analyses of the input chrome-tanned shavings, as well as of the output chromium sludge and protein hydrolysate, are given in the following Table I:

Table I Analyses of chromium the input shavings and the obtained filtrate and filter cake, respectively.

	Chromium shavings	Filtrate (protein hydrolysate)	Filter cake (chromium sludge)
Dry matter	85.80 %	14.00 %	18.42 %
Ash*	9.58 %	5.01 %	26.83 %
Nitrogen*	14.04 %	13.98 %	10.63 %
Chromium*	2.85 %	23 ppm	4.88 %
$MgO$ *	-	1 900 ppm	4.02 %

\*related to the dry matter

All the per cent data mean w/w

#### B. Determination of titration curves

This part included potentiometric titrations of individual components of chromium cake with special focus on the titration curve of magnesium oxide ( $MgO$ ), magnesium carbonate ( $MgCO_3$ ),  $MgO$  in mixture with chromium (III) oxide ( $Cr_2O_3$ ), chromium (III) oxide ( $Cr_2O_3$ ), and magnesium sulfate ( $MgSO_4$ ), respectively. Titrations were carried out with the standard solution of 0.1N  $H_2SO_4$ , on titration apparatus with a 25 ml burette (Fig. 1). The reaction blend was stirred with magnetic stirrer.  $pH$  of the solution was measured with Portable  $pH$  meter CPH 52 equipped with a measuring probe.



Fig. 1 Titration apparatus.

#### C. Kinetics of $MgO$ extraction from the chromium cake

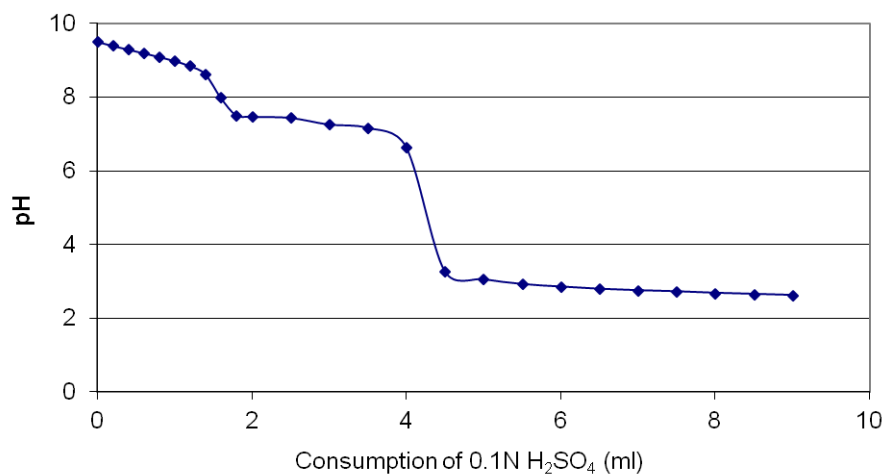
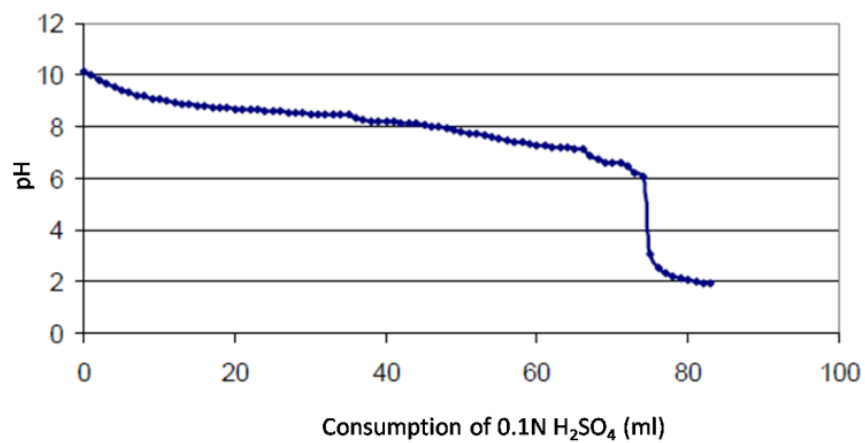
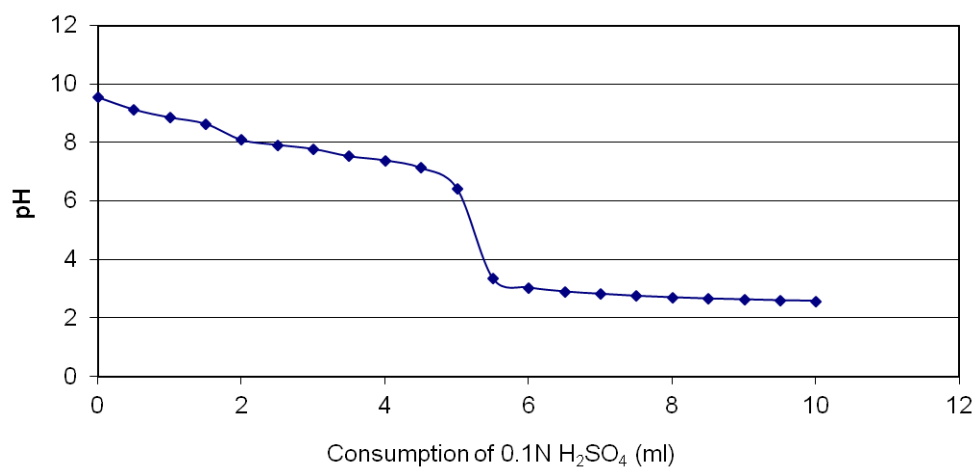
500 ml of a  $H_2SO_4$  solution of  $pH$  4.5 was placed in a beaker and 100 g of the filtration cake obtained in the previous experiment was added. The mixture was stirred intensively during the whole experiment. After stabilization of  $pH$ , additional  $H_2SO_4$  was added to reduce the  $pH$  to the original level of 4.5. The time during which the  $pH$  raised from 4.5 to 5 was recorded, as well as the amount of  $H_2SO_4$  necessary to reduce the  $pH$  to the value of 4.5.

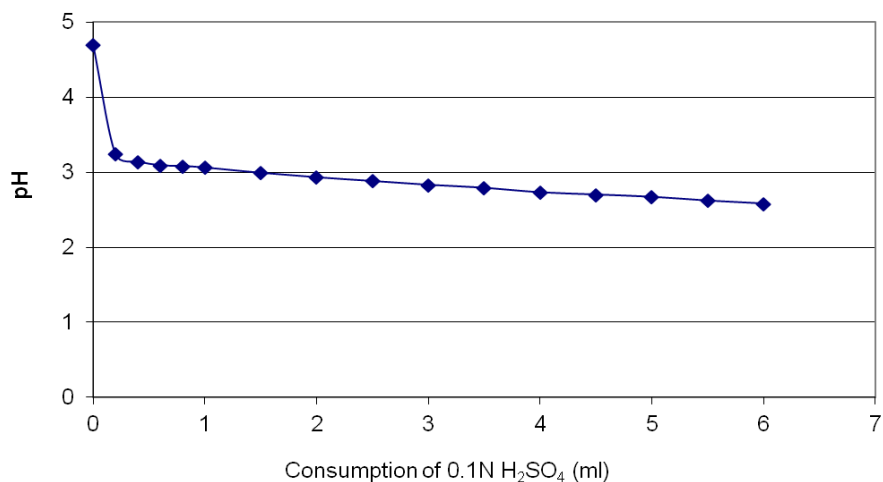
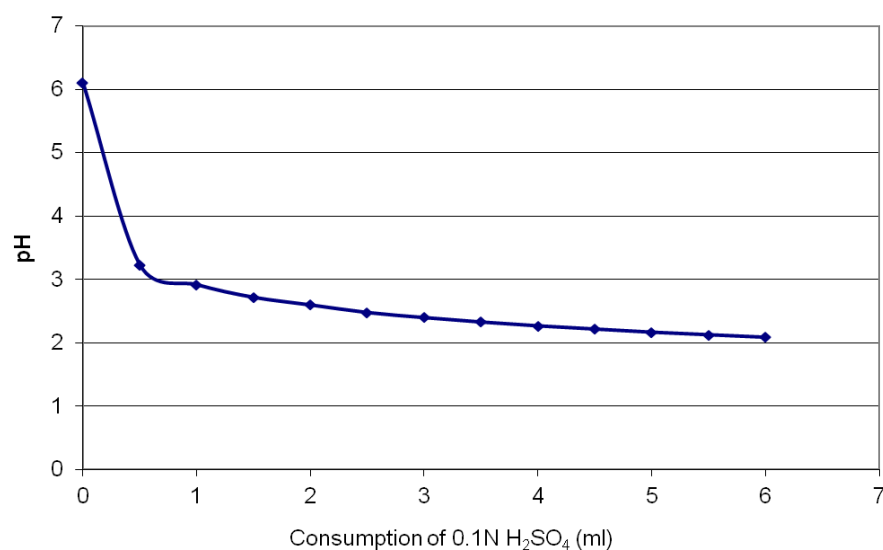
After the addition of filtration cake (*i.e.* after the first  $pH$  stabilization) the  $pH$  of the mixture raised to 9.1. This  $pH$  will be referred to as the equilibrium  $pH_R$  in further calculations.

### IV. RESULTS

#### A. Titration curves

The resulting titration curves of the selected components of the systems are shown in the following Figs. 2-5. An example of a titration curve of  $MgO$  titrated with 0.1N  $H_2SO_4$  standard solution is shown in Fig. 2. An example of a titration curve of  $MgCO_3$  titrated with 0.1N  $H_2SO_4$  standard solution is shown in Fig. 3. Fig. 4 shows resulting potentiometric titration curve of a solution containing only  $Cr_2O_3$ . The result of simultaneous potentiometric titration of a mixture of  $MgO$  and  $Cr_2O_3$  titrated with 0.1N  $H_2SO_4$  standard solution is shown in Fig. 5.

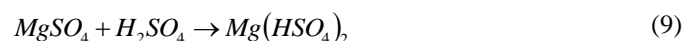
Fig. 2 Titration of MgO with 0.1N H<sub>2</sub>SO<sub>4</sub>.Fig. 3 Titration of MgCO<sub>3</sub> with 0.1N H<sub>2</sub>SO<sub>4</sub>.Fig. 4 Titration of MgO + Cr<sub>2</sub>O<sub>3</sub> with 0.1N H<sub>2</sub>SO<sub>4</sub>.

Fig. 5 Titration of MgO + Cr<sub>2</sub>O<sub>3</sub> with 0.1N H<sub>2</sub>SO<sub>4</sub>.Fig. 5 Titration of MgSO<sub>4</sub> with 0.1N H<sub>2</sub>SO<sub>4</sub>.

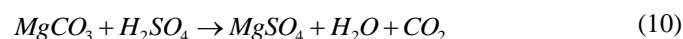
It is apparent from the titration graph in Fig. 2 that there are two equivalence points. This implies that in addition to the reaction of MgO, reactions of other component (components) take place. If we assume that there are no more complex intermediate products, there can basically be two substances, namely magnesium carbonate and magnesium hydrogen sulfate Mg(HSO<sub>4</sub>)<sub>2</sub>. The latter can react with subsequent reaction of magnesium sulfate (MgSO<sub>4</sub>), which was formed after reaction of MgO with sulfuric acid, while magnesium carbonate can be present in commercial MgO (e.g. in cases if commercial MgO is subjected to airborne CO<sub>2</sub>) and react with sulfuric acid resulting in the formation of CO<sub>2</sub> and water.

The possibility of the presence of the said substances can be estimated both from titration graphs and, more precisely, from the mass balance of individual components.

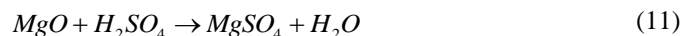
The reaction of magnesium sulfate with sulfuric acid can be depicted by the following scheme:



Magnesium carbonate reacts with sulfuric acid according to (10):



From the consumption of H<sub>2</sub>SO<sub>4</sub> (1.6 ml) in the equilibrium point (pH = 8) from graph in Fig. 2 we determined the amount of MgO spent for the first reaction according to (11) and subsequently (12):



$$m_{\text{MgO}} = \frac{N_{\text{H}_2\text{SO}_4} \cdot V_{\text{H}_2\text{SO}_4} \cdot f \cdot M_{\text{MgO}}}{2 \cdot 1000} = \quad (12)$$

$$= \frac{0.1 \text{ mol} \cdot \text{ml}^{-1} \cdot 1.6 \text{ ml} \cdot 1.074 \cdot 40.31 \text{ g} \cdot \text{mol}^{-1} \cdot M_{\text{MgO}}}{2 \cdot 1000}$$

Where  $N$  is normality of the solution of  $\text{H}_2\text{SO}_4$  [ $\text{mol} \cdot \text{l}^{-1}$ ],  $f$  stands for the factor of sulfuric acid solution [1],  $V$  is the volume of  $\text{H}_2\text{SO}_4$  spent in the reaction [ml] and  $M$  stands for molar mass [ $\text{g} \cdot \text{mol}^{-1}$ ].

The amount of reacted MgO is  $3.46 \cdot 10^{-3}$  g.

Now we calculated mass balances (all figures related to g MgO) for the cases of the reactions of 1) magnesium sulfate to magnesium hydrogen sulfate according to (9), and 2) magnesium carbonate to magnesium sulfate according to (10).

1) The consumption of  $\text{H}_2\text{SO}_4$  in the second equivalence point can be calculated as the difference between the consumption after reaction (11) and the consumption in the second equivalence point, *i.e.*  $4.6 \text{ ml} - 1.6 \text{ ml} = 2.7 \text{ ml}$ . For reaction (9), the amount of reacted  $\text{MgSO}_4$  [g] was calculated according to (13):

$$m_{\text{MgSO}_4} = \frac{N_{\text{H}_2\text{SO}_4} \cdot V_{\text{H}_2\text{SO}_4} \cdot f \cdot M_{\text{MgSO}_4}}{2 \cdot 1000} = \quad (13)$$

$$= \frac{0.1 \text{ mol} \cdot \text{ml}^{-1} \cdot 2.7 \text{ ml} \cdot 1.074 \cdot 120.36 \text{ g} \cdot \text{mol}^{-1} \cdot M_{\text{MgO}}}{2 \cdot 1000}$$

The resulting amount of reacted  $\text{MgSO}_4$  is  $3.49 \cdot 10^{-2}$  g. Related to MgO, the amount of reacted MgO is  $1.17 \cdot 10^{-2}$  g.

2) In this case we assume that the second equivalence point reflects reaction (10). The amount of reacted  $\text{MgCO}_3$  is then calculated according to (14):

$$m_{\text{MgCO}_3} = \frac{N_{\text{H}_2\text{SO}_4} \cdot V_{\text{H}_2\text{SO}_4} \cdot f \cdot M_{\text{MgCO}_3}}{2 \cdot 1000} = \quad (14)$$

$$= \frac{0.1 \text{ mol} \cdot \text{ml}^{-1} \cdot 2.7 \text{ ml} \cdot 1.074 \cdot 84.32 \text{ g} \cdot \text{mol}^{-1} \cdot M_{\text{MgO}}}{2 \cdot 1000}$$

The resulting amount of reacted  $\text{MgCO}_3$  is  $1.22 \cdot 10^{-2}$  g. Related to MgO, the amount of reacted MgO is  $5.83 \cdot 10^{-3}$  g.

Now we calculated the overall amount of MgO in both cases.

1) In the case that the final product is magnesium hydrogen sulfate, the following amount of MgO was spent (15):

$$m_{\text{MgO}} + m_{(9)\text{MgO}} = \quad (15)$$

$$= 3.46 \cdot 10^{-3} \text{ g} + 1.18 \cdot 10^{-2} \text{ g} = 15.26 \cdot 10^{-3} \text{ g MgO}$$

Where  $m_{\text{MgO}}$  [g] stands for the amount of MgO spent on the reaction with  $\text{H}_2\text{SO}_4$  in the first equivalence point,  $m_{(9)\text{MgO}}$  [g] is the amount of MgO spent on the reaction with  $\text{H}_2\text{SO}_4$  in the case that the reaction takes the course according to (9).

2) In the case that the reaction takes the course according to (10), the following amount of MgO was spent (16):

$$m_{\text{MgO}} + m_{(10)\text{MgO}} = \quad (16)$$

$$= 3.46 \cdot 10^{-3} \text{ g} + 5.83 \cdot 10^{-3} \text{ g} = 9.29 \cdot 10^{-3} \text{ g MgO}$$

Where  $m_{(10)\text{MgO}}$  [g] is the amount of MgO spent on the reaction with  $\text{H}_2\text{SO}_4$  in the case that the reaction takes the course according to (10).

Now let us summarize the overall mass balance. A total of 0.02 g of MgO was put into the reaction during titration. The following calculations show the measurement error, *i.e.* the difference between the real amount of MgO entering the reaction and the amount of MgO calculated above for the cases, *i.e.* according to (9) or (10), respectively. The measurement errors for both cases are shown in (17) and (18):

$$\frac{0.02 - 0.0153}{0.02} \cdot 100 = 23.5\% \quad (17)$$

$$\frac{0.02 - 0.00929}{0.02} \cdot 100 = 53.55\% \quad (18)$$

It is apparent from the measurement errors that the reaction of  $\text{MgSO}_4$  to  $\text{Mg}(\text{HSO}_4)_2$  (9) is more likely to take place in the second equivalence point than reaction (10). However, taking into account the relatively high measurement error even in the case of (9), the most probable conclusion is that both substances are present in the solution and react with  $\text{H}_2\text{SO}_4$  to some extent.

This assumption is further supported by the titration graphs of  $\text{MgCO}_3$  (Fig. 3) and  $\text{MgSO}_4$  (Fig. 5). It can be seen in the graphs that titration curves of both substances overlap from a major part within the critical range of pH 7-3. Within pH of approx. 6-3 it is more likely that reaction (9) takes place since it appears like relatively distinct equivalence point and appears in both the titration curve of  $\text{MgSO}_4$  (Fig. 5) and  $\text{MgCO}_3$  (Fig. 3). It is also in accordance with the above balance calculations. However, since there is a distinct second equivalence point in the titration curve for MgO (Fig. 2) at pH of approx. 6.8, certain amount (though probably very low) of  $\text{MgCO}_3$  in commercial MgO cannot be excluded.

### B. Dependence of chromium solubility on pH

The amount of dissolved chromium was calculated for various pH levels according to (5) and the calculations described in the related chapter. For the graph, logarithm scale for the amount of substance of dissolved chromium was used. The result is shown in Fig. 7:

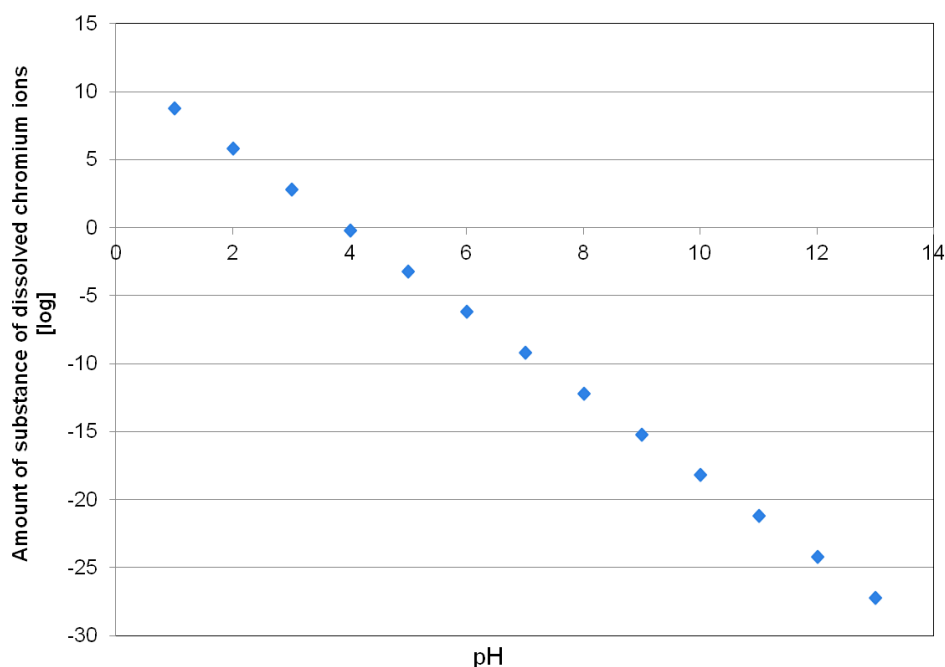


Fig. 7 Dependence of the logarithm of the amount of substance of dissolved chromium on pH.

### C. Kinetic results of the MgO extraction from chromium sludge

The results of the kinetics of the extraction of MgO from the chromium cake with 0.1N H<sub>2</sub>SO<sub>4</sub> are shown in the following Table II.

Table II Results of the kinetic measurement of the extraction of MgO with 0.1N H<sub>2</sub>SO<sub>4</sub> as well as the velocity constants of the reaction of MgO with H<sub>2</sub>SO<sub>4</sub> calculated according to (5).

Measr. No.	Consumption of 0.1N H <sub>2</sub> SO <sub>4</sub> [ml]	Time $\tau$ [s]	Velocity constant [s <sup>-1</sup> ]
1	44.6	53	$2.2 \cdot 10^{-3}$
2	50.6	184	$6.4 \cdot 10^{-4}$
3	54.1	531	$2.2 \cdot 10^{-4}$
4	56.8	1982	$5.9 \cdot 10^{-5}$
5	59.0	10080	$1.2 \cdot 10^{-5}$

It is apparent from Table II that the velocity constants differ within two orders of magnitude. Together with the courses of titration of MgO and MgCO<sub>3</sub> (both reactions ran very slowly and it took a long time for the pH after addition of H<sub>2</sub>SO<sub>4</sub> to stabilize), the results imply that the reaction does not follow the kinetic model presented in Chapter II. Therefore it was necessary to search for mechanisms that could possibly affect the reaction to propose more accurate mathematical description. The most probable phenomenon is diffusion.

To verify whether diffusion can actually take place, we used

the Nernst equation [10]:

$$D_0 = 8.931 \cdot 10^{-10} T \left( \frac{l_+^0 \cdot l_-^0}{l_+^0 + l_-^0} \right) \left( \frac{z_+ + z_-}{z_+ \cdot z_-} \right) \quad (19)$$

Where  $D_0$  stands for diffusion coefficient of electrolyte at infinite dilution [cm<sup>3</sup>·s<sup>-1</sup>],  $l_+^0$  is cationic conductivity at infinite dilution [mhos/equivalent],  $l_-^0$  is anionic conductivity at infinite dilution [mhos/equivalent],  $T$  is absolute temperature,  $z_+$  is the valence of cation and  $z_-$  stands for the valence of anion.

By incorporation the values for H<sub>2</sub>SO<sub>4</sub> [11] into (19) we get:

$$D_{0H_2SO_4} = 8.931 \cdot 10^{-10} \cdot 293 \left( \frac{349.8 \cdot 80.0}{349.8 + 80.0} \right) \left( \frac{2+1}{2 \cdot 1} \right) \quad (20)$$

Diffusion coefficient of H<sub>2</sub>SO<sub>4</sub> at infinite dilution is  $2.55 \cdot 10^{-9}$  m<sup>2</sup>·s<sup>-1</sup>.

Now we need to find out the particle size at which diffusion of H<sub>2</sub>SO<sub>4</sub> takes place and to compare it with the approximate size of particles used in the experiments. We used Fourier equation [12] (Table II, Measurement No.4, *i.e.* 1982 s):

$$Fo = \frac{D \cdot \tau}{a^2} \quad (21)$$

Where  $Fo$  stands for dimensionless time,  $D$  is the diffusion coefficient of a substance [cm<sup>3</sup>·s<sup>-1</sup>],  $a$  is the size of the particle [m] and  $\tau$  stands for time [s].

The calculated size of the particle was  $2.26 \cdot 10^{-3}$  m.

In real conditions, the size of the particles is usually by two orders of magnitude smaller (*i.e.* around  $10^{-2}$  mm), which according to [12] can be applied to our case.

#### V. MATHEMATICAL MODEL OF MAGNESIUM OXIDE EXTRACTION FROM CHROMIUM CAKE WITH SULFURIC ACID

According to the results described above it is highly probable that the extraction of MgO from filtration cake with  $H_2SO_4$  is affected by diffusion. The diffusion for a spherical particle can be described according to [13]:

$$\frac{1}{D} \frac{\partial c(r, \tau)}{\partial \tau} = \frac{\partial^2 c(r, \tau)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r, \tau)}{\partial r} \quad 0 < r < a, \tau < 0 \quad (22),$$

with the following initial and boundary conditions:

$$\frac{\partial c}{\partial r}(0, \tau) = 0 \quad (22a)$$

$$-SD \frac{\partial c}{\partial r}(a, \tau) = V_0 \frac{\partial c_0}{\partial \tau}(\tau) \quad (22b)$$

$$c(r, 0) = c_p \quad (22c)$$

$$c(a, \tau) = \varepsilon c_0(\tau) \quad (22d)$$

$$c_0(0) = 0 \quad (22e)$$

The following dimensionless quantities were introduced for further processing:

$$C = \frac{c}{c_p}; R = \frac{r}{a}; Fo = \frac{D \cdot \tau}{a^2}; C_0 = \frac{c_0}{c_p} \quad (23),$$

where  $Fo$  stands for dimensionless time (Fourier number),  $C$  is dimensionless concentration of the extracted component in the solid phase,  $C_0$  is dimensionless concentration of the extracted component in the solution and  $R$  stands for dimensionless size of a spherical particle.

Through incorporation of the dimensionless quantities in (22) we get the diffusion model in dimensionless form:

$$\frac{\partial C(R, Fo)}{\partial Fo} = \frac{\partial^2 C(R, Fo)}{\partial R^2} + \frac{2 \partial C(R, Fo)}{R \partial R} \quad (24)$$

$$\frac{\partial C(0, Fo)}{\partial R} = 0 \quad (24a)$$

$$-\frac{\partial C(1, Fo)}{\partial R} = \frac{Na}{3\varepsilon} \cdot \frac{\partial C_0(Fo)}{\partial Fo} \quad (24b)$$

$$C(R, 0) = 1 \quad (24c)$$

$$C(1, Fo) = C_0(Fo) \quad (24d)$$

$$C_0(0) = 0 \quad (24e)$$

Analytical solution of (22-24b) was published in [14] for temperature field of a spherical body. After adjustment of the solution for concentration field of a spherical particle we get for the dimensionless concentration of the extracted component in the solid phase:

$$C = \frac{c}{c_p} = \frac{\varepsilon}{Na + \varepsilon} - \frac{2Na}{3\varepsilon R} \sum_{n=1}^{\infty} \frac{\left[ \frac{Na^2}{\varepsilon^2} q_n^4 + 3 \left( 2 \frac{Na}{\varepsilon} + 3 \right) q_n^2 + 9 \right] \sin(R \cdot q_n) \sin(q_n) \cdot e^{-Fo \cdot q_n^2}}{\frac{Na^2}{\varepsilon^2} q_n^4 + 9 \left( \frac{Na}{\varepsilon} + 1 \right) q_n^2} \quad (25),$$

where  $\varepsilon$  stands for porosity [dimensionless] and  $Na$  stands for dimensionless ratio of the volume of extraction solution to the volume of solid phase ( $V_0/V$ ) (so-called soaking number).

Analogously, the dimensionless concentration field of the extracted component in the solution is given by (26):

$$C_0 = \frac{c_0}{c_p} = \frac{1}{Na + \varepsilon} - \frac{6Na}{\varepsilon} \sum_{n=1}^{\infty} \frac{e^{-Fo \cdot q_n^2}}{\frac{Na^2}{\varepsilon^2} q_n^2 + 9 \left( \frac{Na}{\varepsilon} + 1 \right)} \quad (26),$$

where  $q_n$  represent the roots of the following equation:

$$tg(g) = \frac{3g}{3 + \frac{Na}{\varepsilon} g^2} = 0 \quad (27)$$

#### VI. DISCUSSION

The extraction of MgO from chromium sludge was studied. The sludge was prepared by alkaline enzymatic hydrolysis, with MgO as promoter of the reaction. This compound has to be removed after the process to achieve the maximum quality of hydrolysis products. It emerges from few publications dealing with this problem (*e.g.* [3, 7]), that the attempts to remove MgO from chromium cake were not completely successful. The most suitable method so far seems to be MgO extraction by diluted  $H_2SO_4$ , but the efficiency of MgO removal was not 100 % either. The possible mechanisms that might affect the technological method are discussed below.

The titration graphs of individual components of chromium cake were made with the use of potentiometric titrations. The graphs show the equivalence points of the components reaction with  $H_2SO_4$ . We particularly focused on MgO and  $Cr_2O_3$  titrations, because during MgO extraction it is necessary at the



same time to prevent  $\text{Cr}_2\text{O}_3$  from reaction with the acid. It follows from the graph for  $\text{MgO}$  (Fig. 2) that there are either further reactions of the products (e.g.  $\text{MgSO}_4$ ) with  $\text{H}_2\text{SO}_4$ , or the commercial  $\text{MgO}$  may contain  $\text{MgCO}_3$ .

Therefore, more details studies were carried out on the reactions of  $\text{MgCO}_3$  and  $\text{MgSO}_4$  with  $\text{H}_2\text{SO}_4$ . Balance calculations confirmed the possible participation of both compounds in the reaction, with prevalence of the reaction  $\text{MgSO}_4$  to  $\text{Mg}(\text{HSO}_4)_2$ . The occurrence of  $\text{MgCO}_3$  cannot be excluded neither according to the balance calculations, nor to graphs.

One of possible explanations is that it coats the protein molecules and causes diffusion phenomena, particularly the inner diffusion. The diffusion is signalized by:

- Calculation of diffusion coefficient for sulfuric acid, which shows that the real size of molecules in chrome cake would allow diffusion process.

- Calculation of the velocity constant for the reaction of  $\text{MgO}$  and  $\text{H}_2\text{SO}_4$  in the given range of pH.

The kinetics of the reaction shows that the velocity constants differ significantly, which means that the reaction does not run in accordance with kinetics principles. Therefore, the mathematical model was selected for the situation when  $\text{MgO}$  extraction is hindered by the inner diffusion of  $\text{H}_2\text{SO}_4$  into particles. The results can contribute to more efficient processing of chromium shavings. Suitability of this model for  $\text{MgO}$  extraction from chrome cake will be verified by further research.

#### VII. LIST OF SYMBOLS

$C$	Dimensionless concentration of the extracted component in the solid phase	[1]
$C_0$	Dimensionless concentration of the extracted component in the solution	[1]
$D_0$	Diffusion coefficient of electrolyte at infinite dilution	$[\text{cm}^3 \cdot \text{s}^{-1}]$
$D$	Diffusion coefficient of a substance	$[\text{cm}^3 \cdot \text{s}^{-1}]$
$F_0$	Dimensionless time	[1]
$M$	Molar mass	$[\text{g} \cdot \text{mol}^{-1}]$
$N$	Normality of the solution of $\text{H}_2\text{SO}_4$	$[\text{mol} \cdot \text{l}^{-1}]$
$Na$	Soaking number	[1]
$R$	Dimensionless size of a spherical particle	[1]
$a$	Size of a particle	[m]
$k$	Velocity constant	$[\text{s}^{-1}]$
$\varepsilon$	Porosity	[1]
$\tau$	Time	[s]

Other symbols are explained directly in the text.

#### REFERENCES

[1] K. Kolomaznik, M. Barinova, and H. Vaskova, "Chromium VI Issue in Leather Waste – A Technology for the processing of usedleather goods and potential of Raman spectroscopy in chromium traces detection", *International Journal of Mathematics and Computers in Simulation*, vol. 6, no. 5, pp. 447–455, 2011.

[2] O. Kirk, *Encyclopedia of Chemical Technology*, 4th ed., John Wiley & Sons Inc., New York, 1992.

[3] K. Kolomaznik, M. Mladek, F. Langmaier, D. Janacova, and M. M. Taylor, "Experience in industrial practice of enzymatic dechromation of chrome shavings," *JALCA*, vol. 94, no. 2, pp. 55-63, 1999.

[4] L. F. Cabeza, M. M. Taylor, G. L. DiMaio, E. M. Brown, W. N. Marmer, R. Carrió, P. J. Celma, and J. Cot, "Processing of leather waste: pilot scale studies on chrome shavings. Isolation of potentially valuable protein products and chromium," *Waste Manage.*, vol. 18, no. 3, pp. 211-218, 1998.

[5] J. Dolinay, P. Dostalek, V. Vasek K. Kolomaznik, and D. Janacova, "Modernization of control system for enzymatic hydrolysis", *WSEAS Transactions on Systems and Control*, vol. 3, no. 9, pp. 1094–1101, 2011.

[6] L. Macků and D. Sámek, "Two step, PID and model predictive control using artificial neural network applied on semi-batch reactor", *WSEAS Transactions on Systems*, vol. 10, no. 9, pp. 1039-1049, 2010.

[7] P. Mokrejs, D. Janacova, K. Kolomaznik, M. Mladek, and F. Langmaier, "Bath washing of  $\text{MgO}$  from the chrome sludge using diluted sulfuric acid," in *Proceedings of CHISA 2006, 17 International Congress of Chemical and Process Engineering*, Prague, 2006, p. 454.

[8] P. Mokrejs, K. Kolomaznik, M. Mladek, and F. Langmaier, "Study of the kinetics of the production of chromium from enriched sludge" [In Czech], *Chemické Listy*, vol. 98, no. 8, p. 700, 2004.

[9] M. Dvorackova, "Deproteinization of chromium sludges during their recycling" (Dissertation Thesis style) [In Czech], Tomas Bata University in Zlin, Czech Republic, 2005.

[10] W. Nernst, "Zur Kinetik der in Losung befindlichen KSrper.-I. Theorie der Diffusion," *Zeitsch. f. Physik. Chem.*, vol. 2, pp. 613-637, 1888.

[11] R. H. Perry and C. H. Chilton, *Chemical Engineer's Handbook*, 5th ed., McGraw- Hill, New York, 1973. 2640 pp.

[12] K. Kolomaznik, *Modeling of manufacturing processes* (Textbook style) [in Czech]. Brno University of Technology, Brno, Czech Republic, 1990.

[13] S. Paterson, "The heating or cooling of a solid sphere in a well-stirred fluid," *Proc. Phys. Soc.*, vol. 59, pp. 50-58, 1947.

[14] H. S. Carslaw and J. C. Haeger, *Conduction of Heat in Solids*. 2nd ed. Clarendon Press, Oxford, UK, 1959.

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Prof. Kolomaznik was awarded in 1998 the "Rolex Award for Enterprise", for the technology of processing and recycling of potentially hazardous chrome-tanned waste produced by the leather industry. In 2009 he received the ALSOP Award of the American Leather Chemists Association for his long-term contribution to the association and the leather industry.