

Removal of MgO from the Chrome Cake Produced by Enzymatic Hydrolysis of Chrome Shavings

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The tanning industry processes raw hides and converts them into leather, producing considerable quantities of solid and liquid by-products. The solid tanned by-products contain chromium and by-product liquors contain residual chromium. In order to prevent loss of protein material and chrome compounds, technologies were developed for recycling liquid and solid by-products. Recycling solid by-products is being successfully realized through enzymatic hydrolysis. The chrome cake remains an issue as it contains MgO which was used as a promoter in hydrolysis of chrome-tanned solid by-products. High content of MgO in the chrome cake complicates its further use. This presents work addresses the possibility of isolating magnesium, present as hydroxide, from the chrome cake using by-product (spent) tanning liquor. Results showed that it is possible to achieve magnesium removal efficiency up to 70 %.

Key Words: Tannery, Solid by-products, Spent tanning liquor, Chrome cake, MgO, Elution, Pigments.

INTRODUCTION

Considerable effort has been applied recently to resource recovery by processing solid tanned by-products. The technology that has proved to be the most feasible is enzymatic hydrolysis. Some of the first procedures were one-stage degradation of solid by-products in a mildly alkaline environment and moderate temperature (70 °C). Proteolytic enzymes were using in a short reaction time (4-6 h)¹. The isolated chrome-free protein

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solution found commercial utilization as a feed or fertilizer. Molecular mass distribution² ranged from 1,000 to 3,000 Da. One-stage enzymatic hydrolysis technology was gradually improved, particularly to the direction of increased efficiency and convenience, as well as enhancing properties of the main product of enzymatic hydrolysis - a protein hydrolyzate^{3,4}. Advantages of the one-stage process principally include mild reaction conditions, relatively short reaction time and in particular, simplicity of the whole process requiring only one filtering step. Its disadvantage lies in lower quality of protein hydrolyzate. In the two-step conversion of chrome shavings, the cross-linked protein matrix undergoes alkaline disruption initially and is subsequently degraded in a second step by means of the enzyme. The first stage yields high-molecular protein gelatin fractions (applicable to gels, adhesives, photographic substrates, printing, *etc.*) with molecular mass distribution from 10,000 to 20,000 Da. The two-stage process, is also characterized by mild reaction conditions^{2,5}. An alkaline environment for hydrolytic degradation can be produced by MgO alone or by Ca(OH)₂ or various combinations of MgO, NaOH, Na₂CO₃ and Ca(OH)₂. A product of the desired molecular mass may be obtained depending upon the chosen alkaline medium. The advantage of the two-stage process is also a lower total ash content in the gelatin fraction and in the protein hydrolysate. Both attributes arise from employing MgO as the alkali for hydrolysis².

The chrome cake

The chrome cake remaining after two-stage enzymatic hydrolysis of chrome-tanned solid by-products is characterized by low content of total Kjeldahl nitrogen and isolated chromium mostly occurs in the form of Cr(OH)₃. Chemical composition of the chrome cake remaining after enzymatic hydrolysis of chrome shavings according to procedure by Kolomaznik *et al.*⁶ displays limits presented in Table-1.

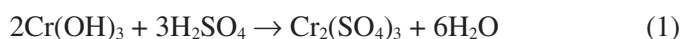
TABLE-1
AVERAGE CHEMICAL COMPOSITION OF THE CHROME CAKE

Parameter	Value (%)
Total solids	16-20
Inorganic solids*	25-35
Total Kjeldahl nitrogen*	0.8-3
Cr ₂ O ₃ *	12-25
MgO*	10-20
Ca, Fe, Al and trace metals oxides*	0.5-2

*Moisture-free basis.

It may be added to cement and mortar⁷ without any adjustment, saving costs of other pigments added. Ash obtained through incineration of the

chrome cake may be used in shoemaking as an additive to polyurethane shoemaking adhesives. Ash containing SiO₂ may replace UV additives that aid when applying these adhesives. Besides, adhesives with added ash have a light to dark green colour, which is an advantage when producing footwear of dark shades⁸. After dissolution in a calculated quantity of sulfuric acid to produce a tanning liquor of 25-30 % basicity (Schorlemmer), it can be used to prepare fresh tanning liquors:



A certain disadvantage here is presence of heterogeneous substances decreasing the quality of liquors thus prepared. Nevertheless, results of physico-chemical tests proved that leathers tanned with reclaimed chromium display a good quality⁹. However, currently, the above cited potential applications of the chrome cake are not widely adopted. The use in preparation of quality pigments is complicated by the presence of MgO whose high content makes processing difficult. For that reason, MgO has to be removed or at least reduced to a level acceptable for processing.

Spent tanning liquors

Globally, spent tanning liquors, predominantly from chrome-tanned leather manufacture, contribute significantly to industrial wastewaters. Composition of typical spent tanning liquors from chrome-tanned leather manufacture^{10,11} is presented in Table-2.

TABLE-2
COMPOSITION OF TYPICAL SPENT CHROME TANNING LIQUORS

Parameter	Value
Suspended solids	1-2.9 g/L
Dissolved solids	4-6 g/L
Total Kjeldahl nitrogen	1.0-1.1 g/L
Fats	~ 0.3 g/L
Chlorides	11-16 g/L
Sulfates	22-23 g/L
Cr(III)	0.3-3.6 g/L
Another metals-Fe(III), Al(III), Mn(II), Ca(II), Mg(II)	0.9-2.1 g/L
pH	3.7-4.2
Colour	Blue-green

Due to the high proportion of chrome-tanned leathers in the market, reducing chrome losses from spent liquors is very significant not merely from the economical but also environmental viewpoint because of land and water source contamination. Chrome reclamation from exhausted liquors is mostly based on precipitation by added alkaline agents, for

example, NaOH, CaO, MgO, NH₄OH, Na₂CO₃^{12,13}. The issue, however, remains of precipitated chromium contaminated with soluble salts, protein fraction (from leather), fats and other impurities reducing its quality. Reclaimed chromium used in preparation of tanning liquors exhibits good tanning properties but these contaminants may persist through to the finished leathers, reducing their quality^{11,14}.

EXPERIMENTAL

The study of MgO removal from the chrome cake utilized the chrome cake remaining after a two-stage enzymatic hydrolysis of chrome shavings and spent liquor remaining after industrial tanning of cow hides. The chemical composition of the chrome cake and tanning liquor is given in Tables 3 and 4.

TABLE-3
CHEMICAL COMPOSITION OF THE CHROME CAKE

Parameter	Value (%)
Total solids	16.4
Inorganic solids*	34.0
Total Kjeldahl nitrogen*	1.4
Cr ₂ O ₃ *	12.5
MgO*	11.5

*Moisture-free basis.

TABLE-4
CHEMICAL COMPOSITION OF SPENT TANNING LIQUOR

Parameter	Value
Total solids	7.1 %
Inorganic solids*	86.7 %
Total Kjeldahl nitrogen*	0.7 %
Cr	1,769 ppm
Mg	692 ppm
pH	4.2
Colour	Blue-green

*Moisture-free basis.

Solids were determined according to IUC 5¹⁵, ash according to ISO 4047:1998¹⁶, total Kjeldahl nitrogen according to ISO 5397:1984¹⁷, Cr₂O₃ according to IUC 8¹⁸, Cr and Mg were determined by flame atomic absorption using GBC 933 AA instrument (GBC Scientific Equipment Pty Ltd., Dandenong, Victoria, Australia) after mineralization of a sample with H₂SO₄ p.a. grade (Sigma-Aldrich).

MgO Removal from the chrome cake

MgO removal from the chrome cake in laboratory conditions was performed by mixing the chrome cake with spent tanning liquor at ambient temperature (22 ± 2 °C) according to scheme shown in Fig. 1. Part of the liquid and solid were subjected to analysis for Mg content. The performance indicator was per cent magnesium eluted by spent tanning liquor from the chrome cake.

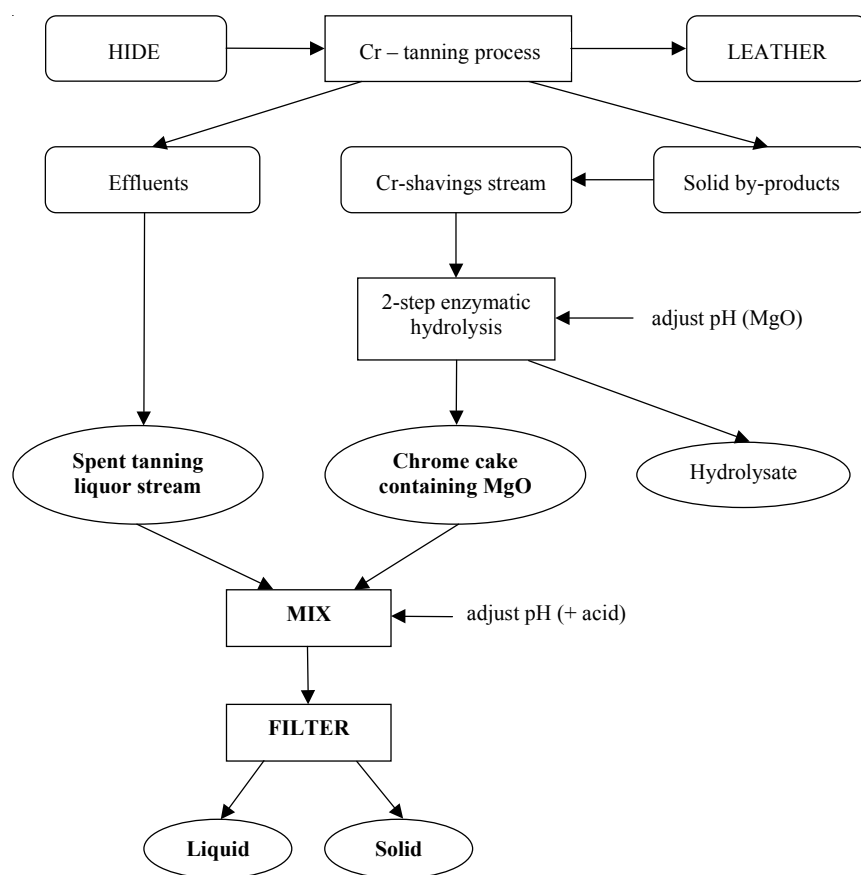
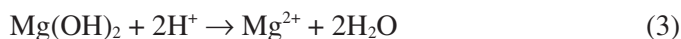


Fig. 1. Flow diagram of magnesium elution from the chrome cake using spent tanning liquor

The principle of removing of MgO contained in the form of hydroxide is based on the large difference in solubility products of chromium hydroxide and magnesium hydroxide¹⁹⁻²¹. Dissolution of MgO in an acidic medium is dissolution of raised $Mg(OH)_2$, according to following equation:



In case free acid is lacking, basicity of potentially present Cr^{3+} salt in liquor grows with increasing pH. Even precipitation of $\text{Cr}(\text{OH})_3$ may take place at a sufficiently high pH level. Fresh liquor displays a basicity of *ca.* 33 %. During tanning and when reducing acidity, its basicity and pH increase. Exhausted liquor usually exhibits basicity \approx 50 %, in some tanning regimes even greater. On achieving a basicity of 70 %, a precipitate is separated from the slurry. Liquors of 70 % basicity are not suitable for starting tanning.

Hence, 1 mol Cr in fresh liquor of 33 % basicity may be basified up to *ca.* 70 % without undesired formation of precipitate. The maximum acceptable change in chromium basicity is then $70 - 33 = 37$ %, which enables to use a simplified symbolic record of MgO dissolution in liquor:



However, if quantity of chromium and possibilities of increasing its basicity are not enough to dissolve the required quantity of MgO, H_2SO_4 has to be directly added, which also possibly serves to decrease basicity to desired level. It is proper to add H_2SO_4 as soon as possible and to dissolve MgO at an elevated temperature under stirring. MgO prepared through thermal breakdown of MgCO_3 reacts with water at a sufficient rate so that initial MgO particles disintegrate to smaller particles of $\text{Mg}(\text{OH})_2$ which, however, during their deposition in filter cake re-crystallize, increase their size and somewhat lessen their reactivity. Solubility of $\text{Mg}(\text{OH})_2$ is very low. The value according to Kotrly and Sucha²² for solubility product *S* at 25 °C is $\text{pS} = 11.12$. From the relation for activity of reacting ions, $[\text{Mg}^{2+}][\text{OH}^-]^2 = 10^{-11.12}$, then follows solubility of $\text{Mg}(\text{OH})_2$ in water = 6.53 mg/L and pH of saturated solution = 10.4. In solutions containing magnesium salt, solubility and pH are lower. When considering dissolution of $\text{Mg}(\text{OH})_2$ in a solution containing 692 ppm Mg, *i.e.* of molar concentration $\text{Mg} = \frac{692 \cdot 10^{-3}}{24.3} = 0.0285$ mol/L, then $0.0285 [\text{OH}^-] = 10^{-11.12}$; thence $[\text{OH}^-] = 1.63 \times 10^{-5}$, *i.e.* pH = 9.2. $[\text{Mg}(\text{OH})_2] = 1/2[\text{OH}^-] = 8.15 \times 10^{-6}$ mol/L and solubility of $\text{Mg}(\text{OH})_2$ is 0.475 mg/L.

The rate of $\text{Mg}(\text{OH})_2$ dissolution obviously decreases with a lower concentration of H^+ because concentration gradients of Mg^{2+} and OH^- on the surface of $\text{Mg}(\text{OH})_2$ particles decrease. Concentration gradient of OH^- however, is kept at a high level by the rapid neutralization reaction of OH^- ions with H^+ ions of the acid environment and flow of OH^- ions potentially brings about forced transport of superfluous Mg^{2+} ions from the surface of $\text{Mg}(\text{OH})_2$ particles. In the environment of a chrome liquor,

however, $\text{Cr}(\text{OH})_3$ starts to precipitate with a rise in pH, *i.e.* in the proximity of particle surface. As the concentration of chrome salt is not high, separated $\text{Cr}(\text{OH})_3$ does not form a compact diffusion barrier even in cases when stirring is not involved. Chromium in the form of insoluble $\text{Cr}(\text{OH})_3$ loses its capability of being easily transported by diffusion. With a diminished inflow of OH^- ions, the potentially formed barrier is dissolved from the side of the acid environment or is torn under the influence of flow in the system produced by different osmotic pressures or by stirring.

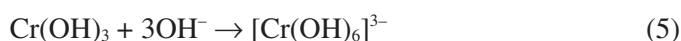
A further slowdown of $\text{Mg}(\text{OH})_2$ dissolution in these systems may be caused by the surface of $\text{Mg}(\text{OH})_2$ particles getting covered with a coat of insoluble magnesium salt, for instance, of Mg soaps of fatty acid or MgCO_3 . Dissolution is also decelerated by sorption of proteins on surface of $\text{Mg}(\text{OH})_2$ particles by means of ionized carboxyl groups $-\text{COO}^-$. The compound in question need not be insoluble, the decisive factor is decelerated transport of OH^- and mainly Mg^{2+} from the surface of $\text{Mg}(\text{OH})_2$ particles.

From analysis of N content in filter cake we may concede that 1 g damp cake might receive not more than *ca.* 16 mg collagen hydrolyzate or in an extreme case even sole glutamic acid. In addition, the quantities of higher fatty acids are certainly several orders less, but with greater doses of liquor can be comparable. Estimating pH value at which $\text{Cr}(\text{OH})_3$ will precipitate in the liquor is somewhat complicated by formation of chromium-sulphate ion complexes. Sulphates have quite high concentration in the liquor, for example, according to Table-2 $[\text{SO}_4^{2-}] = 0.234 \text{ mol/L}$. Considering a Cr concentration of 1,769 ppm in the liquor, *i.e.* 0.034 mol/L and stability constant pK of complex $\text{Cr}^{3+} + \text{SO}_4^{2-} \leftrightarrow \text{Cr}^+\text{SO}_4$ according to Kotrly and Sucha²² pK = -2.6 or pK = -4.6 according to Pitter²³, from

relation
$$K = \frac{[\text{Cr}^+\text{SO}_4]}{[\text{Cr}^{3+}][\text{SO}_4^{2-}]}$$
 . We may calculate that under these conditions

Cr is strongly masked by the produced complex. In case pK = -2.6, concentration of free $[\text{Cr}^{3+}] = 4.21 \times 10^{-4}$, in case pK = -4.6, concentration of free $[\text{Cr}^{3+}] = 4.27 \times 10^{-6}$. From solubility product of $\text{Cr}(\text{OH})_3$, pS = 30.2 according to Patnaik¹⁹ and pS = 28.5 according to Blazej²⁴ we may calculate pH at which $\text{Cr}(\text{OH})_3$ begins to precipitate from a liquor: pH = 5.06 or pH = 5.73 according to Patnaik¹⁹, respectively pH = 5.61 or pH = 6.27 according to Blazej²⁴. We can similarly calculate pH providing either mentioned residual Cr concentrations, *e.g.*, 30 ppm or some other, in a way acceptable, Cr^{3+} concentration. However, residual Cr concentration is strongly affected by potentially present ions producing firm complexes with Cr and thereby efficiently masking it even at a weak concentration. Compounds in question may chiefly be polycarbonic acid, *e.g.*, oxalic acid formed when preparing liquor by reducing dichromate with current organic substances compounds. Stability of complex $[\text{Cr}^{3+} \cdot \text{C}_2\text{O}_4^{2-}]$ has quite

a high $pK = 8$ as given by Kotrly and Sucha²², meaning that masking is more effective than influence of sulphates and is apparent even at very low concentrations of oxalate ion. The oxalate ion is bound to accessible Cr in almost quantitative manner, thereby masking it against precipitation of $Cr(OH)_3$ which takes place only at higher pH levels. However, a substantially increased pH level effects at least partial precipitation of $Cr(OH)_3$ even from complexes if these are not extremely stable. At $pH > 12$, $Cr(OH)_3$ dissolves with formation of chromites.



But such an increase in pH cannot be achieved by means of $Mg(OH)_2$.

Detailed description concerning optimum ratio of spent tanning liquor to the chrome cake to a complete dissolution of MgO contained in the chrome cake is calculated according to a following example. In the case of 100 g of the chrome cake (Table-3) mass of MgO is calculated:

$$m_{MgO} = m_S \cdot m_{TS} \cdot m_{MgO,TS} \quad (6)$$

where, m_{MgO} = mass of MgO (g), m_S = mass of the chrome cake (*i.e.* 100 g), m_{TS} = mass fraction of total solids in the chrome cake (*i.e.* 0.1643), $m_{MgO,TS}$ = mass fraction of MgO in total solids of the chrome cake (*i.e.* 0.1149).

Calculated mass of MgO (1.89 g) is divided by molar mass of MgO (40.3 g/mol) and number of moles are thus calculated ($n = 0.047$). The same number of moles of H_2SO_4 to a complete dissolution of MgO is necessary. In our case, the pH of spent tanning liquor is 4.2 (Table-4) so the concentration of H^+ is calculated:

$$pH = -\log a_{H^+} = -\log 10^{-4.2}; a_{H^+} = 10^{-4.2} \quad (7)$$

$[H^+] = 0.000063$ mol/L, concentration of Cr^{3+} is high-order though: $[Cr^{3+}] = 0.069$ mol/L.

Eqn. 4 assumes that there is effectively evolved 1 mol of H^+ ion per mole of chrome in liquor, so if chrome concentration is 0.069 mol/L, 0.047 mol of MgO corresponds to 1.36 L of liquor. We assumed the density of spent liquor to be approximately 1 kg/L. To sum up, theoretically, 1.36 L of spent liquor to 100 g of the chrome cake should be the minimal ratio to a complete dissolution of MgO which corresponds to 13.6 g of spent liquor to 1 g of the chrome cake. In present case, a maximum 100 surplus of spent tanning liquor was implied.

The experiment was divided into two parts. In first part, 6 various mass ratios of the chrome cake to spent liquor and 3 different elution times were chosen, (Table-5). In the second group of tests, two mass ratios of the chrome cake:spent liquor were chosen and the pH level of the heterogeneous mixture was adjusted to 5 ± 0.1 . Elution times were the same as in the first part of tests (Table-6). During both groups of tests the pH level

was monitored continuously by sinking the pH electrode (pH meter WTW 526, Weilheim, Germany) into the mixed heterogeneous mixture. In the second group of tests the pH level was adjusted in 10 min intervals to 5 ± 0.1 by adding requisite amounts of 10 % H_2SO_4 solution.

TABLE-5
RESULTS OF MAGNESIUM ELUTION FROM THE CHROME CAKE
WITH VARIOUS MASS RATIOS OF THE CHROME CAKE : SPENT
LIQUOR AND AT VARIOUS ELUTION TIMES

Test no.	Mass ratio cake : liquor	Elution time (h)	System pH	Magnesium removed* (%)
1	1:7	0.5	6.26 – 6.84	15
2		1.5	6.28 – 7.34	18
3		3.0	6.43 – 7.37	16
4	1:20	0.5	5.35 – 5.94	39
5		1.5	5.64 – 6.78	41
6		3.0	5.78 – 6.95	57
7	1:35	0.5	4.85 – 5.51	28
8		1.5	4.70 – 5.88	27
9		3.0	4.89 – 5.90	36
10	1:50	0.5	4.39 – 5.00	43
11		1.5	4.38 – 5.28	51
12		3.0	4.56 – 5.31	55
13	1:70	0.5	4.38 – 4.91	49
14		1.5	4.26 – 5.01	53
15		3.0	4.25 – 5.08	70
16	1:100	0.5	4.30 – 4.65	43
17		1.5	4.41 – 4.83	47
18		3.0	4.41 – 4.85	45

*Based on initial content of magnesium in the chrome cake

TABLE-6
RESULTS OF MAGNESIUM ELUTION FROM THE CHROME CAKE
AT SELECTED MASS RATIOS OF THE CHROME CAKE : SPENT
LIQUOR UNDER CONSTANT SYSTEM PH DURING ELUTION AND
AT VARIOUS ELUTION TIMES

Test no.	Mass ratio cake : liquor	Elution time (h)	System pH	Magnesium removed* (%)
1	1:7	0.5	5 ± 0.1	37
2		1.5		39
3		3.0		60
4	1:20	0.5	5 ± 0.1	54
5		1.5		65
6		3.0		66

*Based on initial content of magnesium in the chrome cake.

RESULTS AND DISCUSSION

Magnesium elution from the chrome cake at various mass ratios of the chrome cake to spent liquor and at various elution times are presented in Table-5. Table-6 gives results of magnesium elution from the chrome cake at mass ratio of the chrome cake to spent liquor = 1:7 and 1:20 while keeping pH value of the system constant during elution and during various elution times. Each test was performed in triplicate and the average results of % magnesium removed are reported. The relative standard deviations (RDS) were within $\pm 5\%$.

Fig. 2 graphically shows results of magnesium removal through elution from the chrome cake as a function of chrome cake : spent liquor ratio and at various elution times.

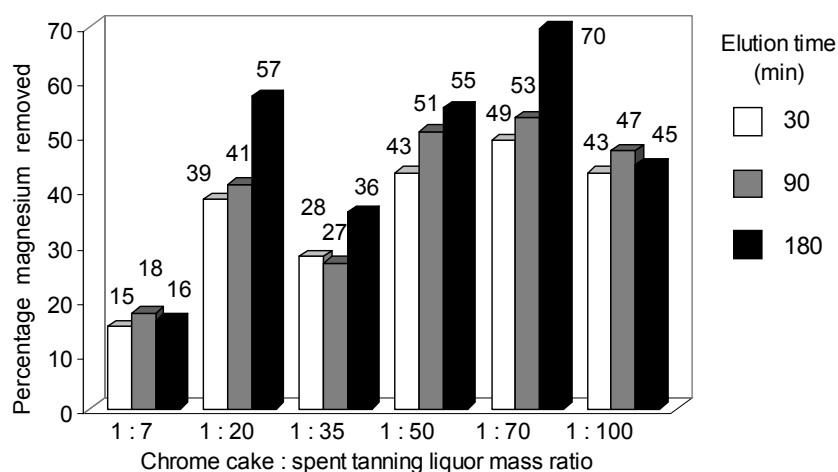


Fig. 2. Percentage magnesium removed from the chrome cake with various mass ratios of the chrome cake to spent liquor at various elution times

At a mass ratio of the chrome cake to spent liquor equal to 1:7, the percentage of magnesium eluted from the chrome cake undergoes almost no change with elution time. After 0.5 h of elution magnesium removal reaches a value exceeding 15%. At 1:20 the percentage of eluted magnesium was higher, growing with elution time and reaching a value above 57% in 3 h. Surprising results are those for the 1:35 ratio, where percentage of eluted magnesium was lower than with ratio 1:20 and maximum was reached after 3 h elution with a value slightly higher than 36%. The ratio 1:50 exhibits a tendency similar to the 1:20 ratio. Highest percentage of eluted magnesium was achieved at a 1:70 ratio, where magnesium removal was higher than 49% at just 0.5 h of elution. Magnesium removal

reaching almost 70 % after 3 h of elution. At the 1:100 ratio overall decrease in the percentage of eluted magnesium appeared. In this sequence the maximum occurred at about 47 % after 1.5 h of elution. Interestingly, the longest elution time was slightly less effective in promoting magnesium elution at this mass ratio.

The anomaly in increase of magnesium removal effectiveness shown by the 1:20 experiment and similarly, the anomaly in decrease of magnesium removal effectiveness shown by the 1:100 experiments (compared to the 1:70 and 1:50 experiments) cannot be precisely explained. Moreover, the results are based on total magnesium balance. Nevertheless, reactivity of $\text{Mg}(\text{OH})_2$ in a long stored filter cake decreases due to $\text{Mg}(\text{OH})_2$ particles enlarging through re-crystallization. If samples of cake are not stored hermetically and not protected against access of atmospheric CO_2 , or possibly react with CO_2 dissolved in the liquor. The particles of $\text{Mg}(\text{OH})_2$ get covered with a coat of MgCO_3 possessing solubility²³ ca. 20 % less than that of $\text{Mg}(\text{OH})_2$, $pS = 8.1$. Breakdown of MgCO_3 requires higher acidity than that sufficient to neutralize $\text{Mg}(\text{OH})_2$, or dissolution requires support by disposing of CO_2 from the whole system. This slows down removal of MgO from long stored samples of filter cake.

Fig. 3 presents bar graphs indicating per cent of magnesium eluted from the chrome cake at two mass ratios of the chrome cake to spent liquor: 1:7 and 1:20. As before, elution times of 0.5, 1.5 and 3.0 h are included. System pH during elution 5 ± 0.1 contrasting to the system without pH adjustment: 6.3-7.4 for the 1:7 ratio and 5.4-7.0 for the 1:20 ratio.

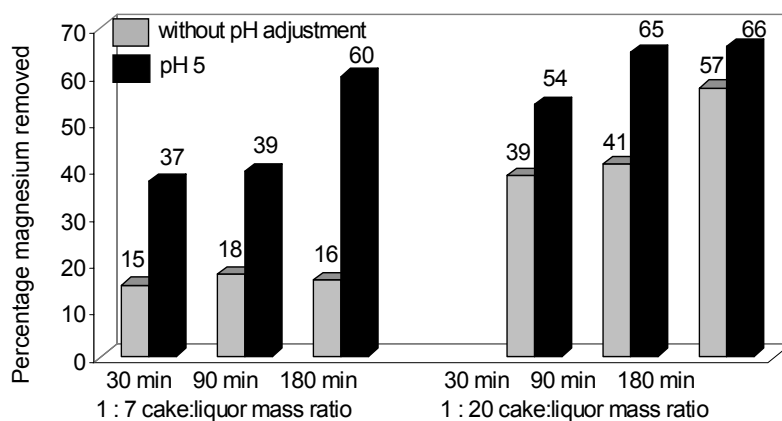


Fig. 3. Percentage magnesium removed from the chrome cake with selected mass ratios of the chrome cake to spent liquor at various elution times with and without pH system adjustment

As can be seen in Fig. 3, maintaining a low pH value of the chrome cake/spent liquor mixture (at a constant 5 ± 0.1 in present case) markedly increased magnesium removal effectiveness from the chrome cake. With 1:7 mass ratio, percentages of magnesium removal were more than two times greater than those from an environment without achieving a pH suitable for magnesium elution. After 3 h, Mg elution reached almost 60 % effectiveness at pH 5. With 1:20 mass ratio, the observed efficiency of Mg elution from the cake was also markedly higher than that from an environment without pH adjustment during elution. Recorded effectiveness after 1.5 h elution was nearly 65 % and increased to more than 66 % after extending the elution time to 3 h. A big difference between the unmodified pH in the 1:7 experiment compared to the 1:20 experiment is due to low spent liquor surplus in the 1:7 experiments. This case confirmed the hypothesis that more spent tanning liquor to the chrome cake is necessary to provide sufficient H^+ ion concentration.

The pH during elution appeared to be an important factor for influencing magnesium elution effectiveness. The comparison of magnesium removal efficiency with and without pH adjustment is intriguing. With cake to liquor = 1:70, elution time of 3 h and no pH adjustment, efficiency was almost 70 %. Comparable magnesium removal efficiency was attained with a much lower ratio of cake to liquor (1:20) while maintaining mixture pH at 5 ± 0.1 (3 h elution). This results is significant cost-effectiveness of the process because the total bath volume is much lower.

The chrome cake, as waste product of enzymatic hydrolysis of chrome-tanned solid shavings, has not yet achieved sufficient utilization. There are methods for processing these materials into $Cr(OH)_3$. This can be combined with virgin basic chrome sulfate to prepare highly economical tanning liquors. According to Cabeza *et al.*²⁵ it is recommended that nitrogen content in the chrome cake, should not exceed 1 %. A more lucrative utilization of the chrome cake consists in procedures leading to the preparation of pigments. Unfortunately, in most cases a negative factor appears, the relatively high content of MgO in the cake (ranging from 10-20 % on a moisture-free basis). The objective of present technology was to reduce MgO content to a level acceptable for processing into a high-quality material. The chrome cake thus produced may serve to prepare yellow pigments according to procedures developed by Tahiri *et al.*^{26,27} and for preparing green and light-rose/pink pigments according to Berry *et al.*²⁸. Both are processes based on incinerating the cake under accurately and carefully defined conditions and with added defined reagents.

Spent tanning liquor, enriched with magnesium (in the form of magnesium sulfate) and rid of residual chrome compounds, pose a much less hazard for the environment. Combining present approach of magnesium

elution with dechromation technology by Kolomaznik *et al.*⁶, a closed cycle is formed, in which chromium compounds are under control and in addition, modification of the solid residue takes place with effective isolation of magnesium compounds.

Conclusion

The present technology combines in untraditional manner a liquid by-product from tanning with a solid residue from enzymatic hydrolysis of chrome-tanned shavings, for complementary recycling these compounds. In the first stage, closed recycling effects the removal of residual chrome compounds from spent tanning liquor at the expense of their increase in the chrome cake. In the second stage, which is the subject of this contribution, MgO content is significantly reduced in the chrome cake, where increased oxide content complicates cake processing. This new described technology is capable of achieving up to 70 % removal of magnesium from the chrome cake. The chrome cake, so treated, may be used in pigment manufacture. The requirement of reducing magnesium to a level acceptable for processing is satisfactory for the majority of cases. At present, multi-stage implementation of magnesium elution is the subject of intensive research in our laboratories, in order to increase the effective magnesium removal from the chrome cake.

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