ALTERNATIVE PROCESS TO RECOVER TANNERY CHROME(III)-EFFLUENTS

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1. INTRODUCTION.

This is a plan to set up an alternative process to recover tannery chrome (III)-effluents. The use of the conventional technique of alkaline-based precipitation (magnesium oxide) of chromium (III) is well known from the bibliography and from daily practice in tanneries worldwide. This technique may in fact represent the cheapest treatment nowadays; however, the latest accurate economic studies have revealed the influence of different parameters that could significantly alter investment costs and thus open a door to other alternative processes. The main problems that the precipitation technique carries with it are the following:

a) the presence of highly masked chrome(III) complexes, difficult to precipitate even in alkaline medium.

b) the speed, and the density of the precipitate can be an important problem. Sometimes, heat energy is required.

c) filtration of the precipitate and subsequent drying out to remove 30% water content of the chrome-cake (different techniques are used).

d) recovered chrome (III) obtained by redissolving the cake with sulfuric acid and final adjustment to 33°Sch basicity can greatly occlude highly masked chrome (III) complexes which, in turn, produce an uneven dyed grain surface of leather; therefore, limiting dyestuff to dark manufactured articles.

Furthermore, energy consumption, the rather long time dependence of the overall process, the simple but numerous stages, and limited coverage fashion catalogue colors comprise the basis from which to offer a possible new alternative process.

This part of the work aims to recover the chromium (1) of wastewater coming from the dechromation process and, at the same time, to get an effluent that can be poured directly without complementary treatments. It is important to give a clearer and detailed idea of the developed process.

1.2. RESIN SELECTION

The resin choice is an important step of the process. In order to the ionic exchange be high, it is necessary that the attraction from the ion selected to the resin choice be important, too.

A number of factors that affect the selectivity of the resin. The resin selectivity in front of diverse ions is classified based on empiric rule series of which the following ones have most interests in the present work.

Related with the temperature, the resin deteriorates and loses its capacity when an abrupt temperature change takes place. (2) During the resin regeneration phase and Cr(VI) to Cr(III) reduction, a great quantity of heat is generated reaching very high temperatures, especially in areas with great quantity of fixed dichromate.

Regarding to time contact, it is important that the resin and the solution have an appropriate time contact; so the exchange is carried out in an effective way avoiding short time contact that has a great importance because would cause a resin wasting.

Resin distribution: When the resin is loaded in the column, the water excess is evacuated assuring that there is no dryness during any moment of the process because repeated cycles of drying and rehydration generate tensions (similar to those taken place in osmotic crashes) and can lead to the resin breakage. Also, the resin should be free of air pockets because these cause preferential ways for which the effluent passes more easily and some areas of the environment could be disabled.
Resin preparation: The resin should be mixed and washed with water to eliminate materials coming from the storage stage, and the wash need to be acidic, which ensures that the exchange resin is an active ionic form. Finally, has chosen the AMBERLITE IRA-96 which is an excellent macroporous resin suitable to fix dichromate ion and resistant to the reduction reaction on a recycling process.

1.3. WASTEWATER OXIDATION PROCESS

The wastewater containing chromium (in their two forms, trivalent and hexavalent) is previously filtered to go through the oxidation step later on with the purpose of obtaining the whole chromium in their hexavalent form for allowing their retention in an anionic exchange resin. The oxidation takes place in basic medium; therefore, a pH 12 should be reached using sodium hydroxide and the oxidation is carried out with hydrogen peroxide that allows a speedy reaction and does not generate any residues. This reaction only forms water as shown in the following reaction.

\[
2\text{Cr}^{3+} + 3\text{H}_2\text{O}_2 + 10\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + 8\text{H}_2\text{O}
\]

The probability of spontaneous oxidising process Cr III into Cr VI is real as from the Gibbs Energies of both reactions. From published thermodynamics functions (Gibbs Energies of Formation):

<table>
<thead>
<tr>
<th>Component</th>
<th>Gibbs Energies of Formation ( \Delta G^\circ )kJmol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cr}_2\text{O}_3 )</td>
<td>-1053</td>
</tr>
<tr>
<td>( \text{OH}^- )</td>
<td>-157.28</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0</td>
</tr>
<tr>
<td>( \text{CrO}_4^{2-} )</td>
<td>-727.85</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>-228.61</td>
</tr>
<tr>
<td>( \text{Cr}_2\text{O}_7^{2-} )</td>
<td>-1301.2</td>
</tr>
<tr>
<td>( \text{H}^+ )</td>
<td>0</td>
</tr>
</tbody>
</table>

Gibbs Energy both reactions:

\[
\Delta G^\circ = -2 \times 727.85 - 4 \times 228.61 - (-2 \times 1053 - 8 \times 157.28) = -461.6 \text{ kJ/mol}
\]

The negative values of the thermodynamic equation proves the possibility of spontaneous oxidation within a wide range of pH. It is a question of the kinetics of the above-mentioned reactions that have been studied in various publications.

The compound acting as oxidizing agent is oxygen that comes from hydrogen peroxide decomposition.

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2 \text{O}_2
\]

During this phase, a brown precipitate is observed, that can be identified as peroxochromates of hard isolation. The reactions\(^{(3)}\) are presented in the next equations.

\[
\text{HCrO}_4^- + 2\text{H}_2\text{O}_2 \rightarrow \left[\text{Cr(O}_2\right]_1^- (\text{OH}^-)^+ + 2\text{H}_2\text{O}
\]

\[
\left[\text{Cr(O}_2\right]_1^- (\text{OH}^-)^+ \right]_{\text{blue}} + \frac{3}{2} \text{H}_2\text{O}_2 + 2\text{OH}^- \leftrightarrow \left[\text{Cr(O}_2\right]_4^{2-} \right]_{\text{brown}} + 2\text{H}_2\text{O}
\]
The blue complex is present in neutral medium and the brown complex in an alkaline medium. This is favored by hydrogen peroxide excess and the basicity of the sample. This reaction is influenced by the oxygen diffusion in reaction medium. As Figure 1 shows in the oxidation process diagram, it is necessary a reagent excess for the formation of the secondary reaction of which it is needed to highlight the following processes: peroxochromates formation and organic matter oxidation.

**Figure 1. Oxidation process diagram.**

<table>
<thead>
<tr>
<th>Na₂CO₃ (40%) pH =12</th>
<th>H₂O₂ (30%)</th>
<th>Acid pH = 3,5-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr³⁺</td>
<td>Cr(OH)₃</td>
<td>CrO₄²⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr₂O₇²⁻</td>
</tr>
</tbody>
</table>

1.4. WASTEWATER LOAD PROCESS

The chromium recovery process is based on the method called ionic exchange where chromium atoms are fixed in the resin. In this phase, chromium is in the chromate form. However, it is better to load chromium in dichromate form because for each possible place of resin two chromium atoms can be fixed instead of one. Therefore, a previous step to the column load is the wastewater acidulation in order to get the dimer formation which has an orange color, instead of yellowish chromate, having a final pH between 3,5 and 4.

\[ 2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O \]

If pH is less than 4, the previous reaction is displaced to the right. Then, it can proceed to the column load with the ionic exchange resin. The most important factor during load is the flow. Keeping in mind that the resin should be always wet in liquid, the flow is fixed in the lowest resin good operation area. The same parameter can be expressed in volume bed by unit of resin for unit of time (BV/h) which can be translate according to the column dimensions. Therefore, the resin volume that the column can contain. The reaction governing the load process is presented in the next equation.

\[ R^{3+}SO_4^{2-} + Cr_2O_7^{2-} \leftrightarrow R^{2+}Cr_2O_7^{2-} + SO_4^{2-} \]

The load is continuous until it is observed the exit of the orange liquid through column bottom indicating that the resin is totally loaded and the dichromate which it is added by column head is no longer fixed in the resin. The results obtained for the load of the resin show that both have an equivalent behavior to similar resins regarding the load capacity.
1.5. CHROMIUM REDUCTION PROCESS

The reduction process of fixed chromium in the resin tends to yield a concentrate chromium liquor using the smallest quantity of reducing agent by substitution of the fixed dichromate in the resin by another anion, and at the same time, reducing the dichromate to trivalent chromium. The reaction takes place in the same column where the load is carried out. The best reducer agent is hydrogen peroxide, but it is necessary to find another one that maintains all the advantages of hydrogen peroxide. Among inorganic reducer agents, their operation is based on the SO$_2$ whose reaction product is sulfate which does not interfere and should be also present in tanning liquors being equivalent for our purpose in this group the sulfite, tiosulfate and disulfite. On the other hand, among the organic reducers, it can be considered the glucose that generates carboxylic groups and would not affect the chromium liquor.

Reduction with hydrogen peroxide.
The reducer agent used is hydrogen peroxide in acid medium. The reaction that takes place is presented in the following equation.

$$Cr_2O_7^{2-} + 8H^+ + 3H_2O_2 \rightarrow 2Cr^{3+} + 7H_2O + 3O_2$$

$$\Delta G_f^\circ = -2 \times 1301.2 - (-2 \times 1053 - 2 \times 228.61) = -39.18 \text{kJ/mol}$$

for acid medium.

The empty places of the dichromate are occupied by sulfate groups coming from the added sulfuric acid. The obtained liquor is concentrated enough, and also rich in sulfates. The reaction in the column can be controlled visually because forms a front that gradually changes its color from orange to green. The next step is to carry out series of washes with water and sulfuric diluted to recover the maximum quantity of chromium, and at the same time, to regenerate the resin.

Reduction with sodium disulfite.
The method of obtaining chromium liquor with disulfite is very similar to the one using the sulfite. In this case, disulfite reacts with acid forming sulfate that acts as reducer and yields bigger quantities of sulfates. Next equation shows the global reaction that governs the process.

$$2Cr_2O_7^{2-} + 3S_2O_5^{2-} + 10H^+ \rightarrow 5H_2O + 6SO_4^{2-} + 4Cr^{3+}$$

This reduction generates an important amount of complex and neutral salts. The experience shows that the reaction could be developed in cold and also without using sulfuric acid.

Reduction with glucose.
This is one of the most widely used reduction methods more widely used in the chromium recovery. In this reaction, glucose is not completely oxidized to carbon dioxide, but some intermediate compounds are formed, generally organic acids that play an interesting role because of their influence diminishing the basicity and masked effect on chromium. The following equation shows the reaction when the glucose suffers a complete oxidation.

$$4Na_2CrO_4 + 12H_2SO_4 + C_6H_{12}O_6 \leftrightarrow 8Cr(OH)SO_4 + 4Na_2SO_4 + 6O_2 + 14H_2O$$

The operation form has an important significance because the tanning properties of the resulting liquors. The masked effect increases as the quantity of glucose is increased favoring the formation of organic acids. In contrast, the temperature reduction makes diminishing the basicity. One problem that arises when using this method is the doubts about if it is much better adding glucose to the acid-dichromate mix or adding acid to the glucose-dichromate mix.
2. EXPERIMENTAL PART.

2.1. EQUIPMENT AND REAGENTS USED.

The smallest volumes of reagents and effluent that are used characterize the work to laboratory scale. Both, reagents and effluent, do not overcome 200 ml.

The equipment used during the experiments were a laboratory column, a decanting funnel, and pH-meter, which are described in appendix B.

The reagents used are the following: hydrogen peroxide, sulfuric acid, sodium hydroxide, sodium disulfite, glucose, sodium carbonate, hydrochloric acid. The same one are described in appendix C.

2.2. RESIN AMBERLITE IRA -96. CHARACTERISTIC

The resin used for the ionic exchange experimental tests is AMBERLITE- IRA-96 (Rohm and Haas) whose characteristics are presented in chart 5.1, meanwhile Table 1, summarizes the theoretical operation conditions.

| Skeleton | Styrene and divinylbenzene copolymer. |
| Functional group | Quaternary amine. |
| Physic appearance | Obscure sphere. |
| Freed ionic shape | Free base. |
| Total exchange capacity | 1,25 eq/L (B.L form). |
| Humidity retention | 57-61% (B.L form). |
| Density | 1,05 (B.L form). |
| Apparent volumetric mass | 670 g/L (B.L form). |
| Granulometry | 0,3 a 1,2 mm of diameter. |
| Maximum reversible swelling | BL- SO₄²⁻: 15 % |
| pH range | 0 – 8 |
| Chemistry resistance | Insoluble in acids and diluted bases also in usual solvent |

Tabla 2. Operation optimal condition.

| Maximum temperature tolerate | 100°C. |
| Bed minimum height | 700 mm. |
| Service flow | 5 to 40 Vol/h. |
| Maxim lineal velocity | 50 m/h. |
| Regenerating agent | NaOH, NH₄OH, Na₂CO₃, H₂SO₄ |
| Regeneration value | 120% from theoretic. |
| Regeneration flow | 2 to 8 Vol/h. |
| Minimum time contact | 30 min. |
| Concentration | 2 to 4%. |

The resin has a half bacisity absorbing all strong acids; it has an excellent exchange capacity and effective elution. The ionic form of the resin is sulfate and, therefore, the most appropriate regenerative agent is sulfuric acid.
2.3. SAMPLE PREPARATION.

**Oxidation wastewater:** The oxidation wastewater contains chromium in chromate form. In order to increase the effectiveness of the ionic exchange, chromate should be transformed into dichromate. This way allow to fix a bigger quantity of chromium (two chromium atoms for each molecule of dichromate fixed) when a pH 3 is reached and it is possible to eliminate most of the carbonate present in wastewater in carbon dioxide form reducing the competition of the dichromate with other ions. Another reason for transforming chromate into dichromate is that the pH of wastewater oxidation (pH 10) can damage or destroy the resin (Hoffman degradation). Because of this fact, when the reaction is carried out, it is necessary to diminish the pH adding sulfuric acid until wastewater reaches pH 3; it is a safe way of converting all chromium into a dichromate form and great part of carbonate will have been eliminated. Finally, the wastewater is filtered to separate all non-dissolved substances like carbonate, skin remains, etc.

**Reduction wastewater.** The wastewater reduction process helps to convert the hexavalent chromium in form of Cr(III)\(^{15}\).

2.4. WASTEWATER LOAD AND REDUCTION

The process completed in the ionic exchange column tries to purify the oxidized wastewater.

For keeping the resin humid, the effluent has to go through the column at the same speed that is evacuated. When the dichromate is fixed on the resin, it is possible to observe the color change passing from beige to orange, and it is crucial that the reaction front moves forward homogeneously avoiding preferential pathways.

**Methodology of the process:**

All the experiments follow the same method except the reducer agents which are added according to their characteristics\(^{14}\). For each reducer, similar quantities of resin are loaded. The phases to keep in mind are as follows: resin fitting up, resin column load, column load and reduction with reducer agent.

**Resin fitting up:**

Resin hydration should take place before the bed in the column, because the pressures created during water absorption can break the column. The next step is adding the appropriate quantity of resin in sulfuric acid dissolution at 20\% (20 g. of resin for 100 ml) and leave during 24 hours.

**Resin column load:**

Fill in the column until half capacity (45 ml of humid resin) but the height varies depending on the disposition and the filled form.

This first phase is very important because a good resin distribution helps its use and increases its effectiveness. The resin in suspension is loaded in the column and the steps are as follows:

- Adding the resin suspension slowly through the column head.
- Eliminating the water excess through the column bottom.
- Avoiding the liquid level is smaller than the resin level.
- Adding the resin in the column in this way: washing resin with successive volumes of water in order to soften the strongly acid pH.


2.5. FLUIDIZATION SYSTEM.

Load the resin in the column with oxidized wastewater to prevent the resin dries off using a decanting funnel in order to control the load speed that it is of vital importance, whereby it is necessary to maintain a minimum flow (4 ml/min). The load should stop when observing the elution of an orange solution through the column bottom. The reducing agents used in the experiences are hydrogen peroxide, sodium disulfite and glucose.

As explained above, during the load process the column is charged with resin. Once the resin has been loaded (retaining the dichromate), it is sent to a sleeved reactor to carry out the reduction of the dichromate to Cr$^{3+}$ and thus obtain the liquor of the recovered chrome, as desired. The transfer of the resin is done by fluidization. This system consists in introducing a current of water through the bottom of the column, causing the resin to rise due to its low density, that is, the resin is pulled by a current of water toward the head of the column. The system for extracting the resin is shown in Figure 2. Resin fluidization scheme.

As Figure 2 shows, a current of compressed air is also introduced to aid the fluidization of the column. The current of air aids the compressed resin to separate, this helping the fluidization. A current of resin and water is obtained from the top of the column. This current must be filtered to separate the resin from the water, and the resin can later be treated as necessary.

2.6. FLUIDIZATION MECHANISM.

Fluidization is the process by which a bed of solid particles, submitted to the drag of a rising fluid, itself behaves like a fluid (is fluidized). Fluidization can be divided into two main types:

1. Bubbling fluidization: when the particles allow bubbles in the fluid to pass, they rise, but then fall back. Particle agglomerations are formed and the particle bed is not fluidized.

2. Particulate fluidization: the particles separate from each other, rising with the fluid, and great but uniform expansion is produced in the bed at high velocities. The particle bed is fluidized.

Generally, one type of fluidization or the other is obtained based on the flow drag and the size of the particles to be fluidized. Beds of large particles, fluidized by a liquid, tend to produce the second type of fluidization. An equation can be obtained for the minimum fluid velocity by taking the fall in pressure through the bed as equal to the weight of the bed per unit area of the cross section, taking into account the flotation force of the fluid displaced.


\[ \Delta P = \frac{g}{g_c} (1 - \varepsilon)(\rho_p - \rho)L \]  
Eq. 3.1

For the incipient fluidization (the bed is on the point of being fluidized) \( \varepsilon \) is the minimum porosity \( \varepsilon_m \) (if at the same time the particles are porous, \( \varepsilon \) is the external fraction of the voids of the bed bed). Therefore:

\[ \frac{\Delta P}{L} = \frac{g}{g_c} (1 - \varepsilon_m)(\rho_p - \rho) \]  
Eq. 3.2

The Ergun equation for the pressure drop in packed beds can be rounded off to obtain:

\[ \frac{\Delta P \cdot g_{c}}{L} = \frac{150 \cdot \nu \cdot V_{O}}{\phi_{S}^{2} \cdot D_{p}^{2}} \frac{(1 - \varepsilon)^{2}}{\varepsilon^{3}} + \frac{1,75 \cdot \rho \cdot V_{O}^{2}}{\phi_{p} \cdot D_{p}} \frac{(1 - \varepsilon)}{\varepsilon^{3}} \]  
Eq. 3.3

Applying Eq. 3.3: at the point of incipient fluidization, a quadratic equation is obtained for the minimum fluid velocity \( V_{CM} \):

\[ \frac{150 \cdot \nu \cdot V_{OM}}{\phi_{S}^{2} \cdot D_{p}^{2}} \frac{(1 - \varepsilon)}{\varepsilon_{M}^{3}} + \frac{1,75 \cdot \rho \cdot V_{OM}^{2}}{\phi_{p} \cdot D_{p}} \frac{1}{\varepsilon_{M}^{3}} = g(\rho_p - \rho) \]  
Eq. 3.4

For small particles, only the laminar flow term in the Ergun equation is important. for \( N_{Re, p} < 1 \), the minimum fluid velocity equation becomes:

\[ V_{OM} = \frac{g(\rho_p - \rho)}{150 \cdot \nu} \frac{\varepsilon_{M}^{3}}{(1 - \varepsilon_m)} \frac{\phi_{S}^{2} \cdot D_{p}^{2}}{\phi_{p} \cdot D_{p}} \]  
Eq. 3.5

The equations obtained for the minimum fluid velocity are applicable both to liquids and to gases, but above \( V_{CM} \) the appearance of the fluidized beds differs notably for liquids or for gases. For the case of particulate fluidization bed expansion is uniform, and the Ergun equation, which is applicable to the fixed bed, one would expect the approximate form for the lightly expanded bed to continue to be fulfilled. Admitting that the flow between particles is laminar, and using the first term of Eq. 3.3, we obtain the following equation for the expanded bed:

\[ \frac{\varepsilon_{M}^{3}}{1 - \varepsilon} = \frac{150 \cdot \nu \cdot V_{O}}{g \cdot (\rho_p - \rho) \cdot \phi_{S}^{2} \cdot D_{p}^{2}} \]  
Eq. 3.6

The height of the expanded bed can be obtained from the values of \( \varepsilon \) and the values of \( L \) and \( \varepsilon \) for the incipient fluidization, using the equation:

\[ L = \frac{1 - \varepsilon_{M}}{1 - \varepsilon} \]  
Eq. 3.7

For the particulate fluidization using large particles in water, it is to be expected that the expansion of the bed would be greater than that in Equation 3.6, since the drop in pressure partly depends on the kinetic energy of the fluid and a greater increase of \( \varepsilon \) is required to compensate a determined percentage of increase in \( V_{CM} \). The expansion data can be correlated via the empirical equation proposed by Lewis, Gilliland and Bauer:

\[ V_{O} = \varepsilon^n \]  
Eq. 3.8
The data from the many investigations indicate that the existing correlation between $V_{CM}$ and $\epsilon$ for different particle diameters can be approximated pretty adequately through a straight line. The slopes of such straight lines varied from 4.5 in the laminar region to 2.5 for high Reynolds numbers; through a graphic correlation proposed by Leva\textsuperscript{(17)} $m$ can be estimated from the Reynolds number: Figure 3 : Exponent of correlation for the bed expansion.

To predict the expansion of the bed, we estimate $m$ using the Reynolds number for the minimum velocity of fluidization and apply Equation 3.8 either directly or as a ratio.

2.7. CALCULATION OF FLUIDIZATION FOR THE PILOT PLANT.

The fluidization of the ion exchange resin in the pilot plant is done with water, introduced through the bottom of the column, as shown in Figure 2. This flow of air was thought of for the topping up of the resin, both during the process of fluidization and during the reduction reaction. However, it was not necessary to use it in the fluidization, since the water current alone was enough to fluidize the resin. In what follows, we show the technical parameters needed to calculate the fluidization of the ion exchange resin. The resin parameters were obtained from the manufacturer’s specifications. The parameters of calculation are:

- Liquid flow: 3000 l/h according to pump specifications, valve regulated.
- Diameter of the column: 0.15 m
- Density of the liquid: 1000 kg/m$^3$
- Viscosity of the liquid: 0.012 P
- Density of the solid: 1050 kg/m$^3$
- Particle diameter: $0.3 \cdot 10^{-3} \text{ – } 1.2 \cdot 10^{-3}$ m ($D_{media} = 0.75 \cdot 10^{-3}$ m)
- Bed height: 0.7 m
- Height of raise necessary for spillover: 1.25 m
• Spherical particles $\phi_s = 1$, $\varepsilon_M = 0.4$

In the previous parameters, it is possible to observe how the ion exchange resin particles have been supposed to be spherical, taking as value of sphericity $\phi_s = 1$ and as value of minimum porosity for fluidization $\varepsilon_M = 0.4$. From Equation 3.4, and choosing as particle diameter the average value of the particles ($D_{\text{medio}} = 0.75 \cdot 10^{-3}$ m),

$$\frac{150 \cdot (0,012)}{(0,075)^2} \cdot \frac{V_O}{0,6} + \frac{1,75 \cdot (1,0)}{0,075} \cdot \frac{V_O^2}{0,43} = 980 \cdot (0,050)$$

Eq. 3.9

Solving quadratic equation Eq. 3.9 yields a value for the minimum velocity of $V_{CM} = 0.16 \cdot 10^{-3}$ m/s. For this value of $V_{CM}$

$$N_{Re,p} = \frac{0,075 \cdot 0,016 \cdot 1,05}{0,012} = 0,105$$

From Figure 4, $m = 4$. According to Equation 3.8,

$$\left( \frac{\varepsilon}{\varepsilon_M} \right)^4 = \frac{V_O}{\bar{V}_{OM}}$$

Eq. 3.10

From here it is possible to calculate the minimum flow velocity (and thus the flow rate) necessary to make the resin flow from the top of the column. The height of the column is 1.25 m., which makes it necessary to raise the resin to this height. From Equation Eq. 3.7,

$$1250 = 700 \frac{1-\varepsilon_M}{1-\varepsilon} \Rightarrow \varepsilon = 0,66$$

Eq. 3.11

From the value of $\varepsilon$ and applying Equation 3.10 we get $\bar{V}_O = 1,21 \cdot 10^{-3}$ m/s. Since the inside diameter of the column is known, it is possible to calculate the minimum flow of liquid necessary, obtaining a value of 77 l/h. This obtained flow value is obviously ridiculous, that is to say, far lower to that available in the pilot plant, which is regulated by the flow of the service pump (3000 l/h). In view of all of this, it is logical to expect that the fluidization that is produced should be in particles and that the resin should exit without any problem through the top of the column. However, this operation must be carried out with great care, attempting to regulate minimally the service pump flow, since the fluidization would otherwise be excessively brusque.

2.8. REDUCTION IN A BATCH SYSTEM.

2.8.1. DESIGN ANTECEDENTS

In previous studies, the final step of the process has consisted in a reduction done in situ, that is, in the same column where the load was developed. This in situ reduction, working on a pilot plant scale, carries with it certain problems, both of the technical and the safety type. These problems are due mainly to the lack of visibility the column causes, since it was designed using an opaque material, as well as the lack of space inside the column for the expulsion of the gases produced by the reduction of the $\text{Cr}_2\text{O}_7^{2-}$ to $\text{Cr}^{3+}$.

To reduce the technical and safety problems to the minimum, we decided to design a system that makes it possible to extract the resin from the inside of the column at any time and without needing to dismantle it. It was also necessary to build a new sleeved reactor capable of supporting the
reduction in its interior since, during the reduction, a reaction heat is generated that must be eliminated. All of these variations in the process and in the design were introduced over the course of the work. These variations made it necessary to modify the plans previously drawn up for the pilot plant as well as the operation manual for the process. All of these changes will be reflected in the course of the present paper; however, it is important to note that the new modifications and specifications will not in themselves make up an entity but should rather be understood as an annex to the work in question. Likewise, the modifications and variants introduced into the process due to the operative experience in the pilot plant should not be understood as a modification of the overall process, which, definitively, goes on maintaining its main framework. The variants introduced in the process will modify the scheme of the previous process; therefore, the single variation introduced is produced in the reduction step of the dichromate to trivalent chrome. More than a variation, this should be understood as an alternative pathway, since the tests previously carried out by way of the on-column reduction gave very positive results, both in the laboratory column and in the pilot-plat scale. However, due to the lack of security involved in carrying out this type of in situ reduction in the pilot plant, we decided to seek an alternative to this method. The main motivations that induced the variation in the way of reducing the dichromate to Cr³⁺ is set out in the following points:

1. **Lack of visual control over the reduction reaction.** Due to the high cost supposed by the construction of the glass column, it was necessary to make the column of stainless steel, taking as a logical consequence the loss of visibility inside the column. This fact totally impeded any visual control over the reduction reaction.

2. **Lack of control over the addition of the reagents.** The lack of visibility in the reaction also meant not being able to observe the front of the reduction reaction, and, as a consequence of this, the addition of the reduction agents could not be adequately carried out.

3. **Low control of the temperature of the reaction.** The physical form of the column, as well as its inaccessibility at certain points (bottoms of the columns), did not allow an efficacious control of the temperature of the reaction, an important parameter for assuring the life of the resin, and for gaining a better knowledge of the reaction.

4. **Lack of security for the operator.** The reduction reaction is produced in an extremely violent way, and this, along with the lack of space inside the column for elimination of the reaction gases, makes the reduction an unsafe one in its development.

5. **Test of other reduction methods.** The “in situ” reduction in the column had been tested previously in other works, yielding very good results. It was thus left to carry out the reduction outside the column, in a stirred reaction adapted to this end.

All of these factors taken together provided the impulse for the search for new reduction systems, varying both the reduction reagents and the way the reaction was done. This search centered on reduction systems, either via new reagents or the way of developing the reaction itself, which met the following conditions:

**Process conditions:**

1. The temperature of the reduction must not in any case be above the maximum allowed by the resin (approx. 90 °C).

2. The temperature of the reduction must not involve any risk for the operator carrying it out.
Figure 4: Chromium recovery by reduction in a sleeved reactor.

- Conditions for the reagents

3 The reagents employed in the reaction must be as cost effective as possible, since one is trying to develop a process on the industrial level; however, it must be clear that at this point we did not seek an optimization of the cost of the process but only tried to avoid an excessive cost of said process.

4 The reagents employed in the reduction reaction must be compatible for later uses with the recovered Cr$^{3+}$, that is, they must not influence the tanning process for which this Cr$^{3+}$ will be used, unless such influence is positive.

Carrying out the process in a stirred reactor proved to be the simplest manner to accomplish the previously described aims of the process. With this type of reduction, the visibility problems presented by the column are eliminated, as is the formation of pockets of gas inside the resin during
the reduction. However, the pilot plant was not adequate for carrying out tests of this type, which made it necessary to introduce some new elements and to modify others already present. The search for new reducing agents was done by bibliographic research, which led to processes used in the tanning industry. Through these, we obtained trivalent chromium for tanning from hexavalent chromium salts. It was then necessary to use in these processes reduction agents that were capable of reducing the hexavalent chromium to trivalent chromium. Additionally, however, these reducing agents must not influence in any way the physical aspect of the skins once tanned. These reducing agents used in this type of processes were offered as ideal candidates to be employed in the development tests.

**Reduction with hydrogen peroxide:**

In acid medium the hydrogen peroxide acts as reducer, which presents a high reaction kinetics and its excess once the reaction is over, can be eliminated easily. The reducing mix is in a ratio 1:1 (H₂SO₄:H₂O₂). The acid prepares the reaction medium and adapts the resin ionic form. The 50% sulfuric acid solution and 30% hydrogen peroxide are used.

The methodical process followed in this part are:

- For preparing the 50% sulfuric acid solution, one must take 520 ml. of acid at 96%, and later adding 480 ml of deionized water.
- Next, mix hydrogen peroxide and sulfuric acid solution in ratio 1:1.
- Add the mixed solution to the resin in order to mix all reagents.
- Finally, eluting and washing the resin inside the column, carrying out two washes for each sample.

**Reduction with sodium disulfite:**

The reduction is carried out using the following proportions: for each 100 g of dichromate, 132 g. of sodium disulfite and 113 g. of sulfuric acid (96%), carrying out the corresponding figure out of wastewater.

The methodical followed in this part are:

- First, dissolve disulfite in water, measure the necessary acid and dilute with the corresponding quantity of water.
- Second, add the disulfite solution to the resin and shake until obtaining a mixture of all reagents.
- Third, add the acid in a controlled way and let the reaction evolves.
- Fourth, Elute and wash the resin inside the column being necessary to carry out two washes for each sample.

**Reduction with D-glucose:**

The reduction is carried out according to the following proportions: for each 100 g. of dichromate, 12 g. of glucose and 136 g. of sulfuric acid (96%). The water quantity is the necessary to dissolve the glucose.

The methodical part proceed as follows:

- The first stage is dissolving the glucose in the necessary quantity of water and preparing the sulfuric acid required.
- Next, add the acid to the resin, shake the mixture and observe and note that increasing the temperature helps the reaction.
- Add the glucose, but if the reaction does not reach the suitable temperature, add some concentrated sulfuric acid and leave the reaction proceeds.
- The last step is continuing the elution and washing the resin inside of the column. In this case, two washes are carried out: the first one with sulfuric acid at 20% and the second with water.

In order to recover the chromium fixed in resin, it is necessary to proceed an elution: the eluent (reducer mix) is added by the column head and the load speed should be smaller for avoiding that the reaction be violent.
The reduction reaction is exothermic, so it is necessary to connect the refrigeration system and load the reducer mix slowly (5 ml/min.). At the same time that the reducer solution is being loaded, the effluent it is evacuated by column bottom, avoiding the resin be dried and making the reaction less violent. When the first green drop through the column bottom comes out, the flow control valve must be closed and the load ends.

As the reaction goes through, the resin returns to its natural color, while the colorless eluent changes to a green blue color. This color change proves the presence of Cr(III) in dissolution. The acid medium makes possible the reduction reaction separating the chromium of the resin and the return of resin to its ionic initial form. The volume of used eluent used agrees with the volume of the worked resin; avoiding a violent reaction.

**Washed:**
To elute the whole fixed chromium, it is necessary to arrange and prepare the resin for later uses. The resin should recover its initial form. Therefore, the sulfate groups should be recovered by means of series of washes with sulfuric acid, and later a rinsing with water in order to leave the resin at pH 3. Two washes with sulfuric acid (20%) are carried out. The washing time is 15 minutes approximately. Simultaneously the cleaning solution is added, 50 ml. of the reducer solution is evacuated.

**Rinsing:**
In this part of the process, the water should be strongly basic (pH 10) for increasing the pH of the resin using a small volume of water. The alkaline water is prepared with NaOH (pH 10) in order to increase the resin pH and use smaller quantity of water.

**2.8.2. WASTEWATER CHROMIUM CONCENTRATION**

This new method is based on the dechroming of the chrome-tanned wastes process in order to isolate a new type of biopolymers. This method is based on the following steps:

1. filtration of tannery effluents, if necessary.
2. oxidation of the chrome (III) to chrome (VI) by the action of hydrogen peroxide in alkaline medium.
3. elimination of the excess of hydrogen peroxide by continous stirring of the oxidized effluent.
4. acidification with sulphuric acid to a pH : 2 – 3, to favour the formation of the dichromate anion, with higher fixation rate onto an ion-exchange resin.
5. Reversible binding to a resin matrix of a macroporous anion exchange resin, type : Amberlite IRA96. This can be considered as a column ion-exchange chromatography step.
6. once the resin is completely saturated with dichromate anion is transported with a conveyor to a stirred tank where will be submitted to a total reduction to chrome (III), by the action of hydrogen peroxide or sodium bisulphite in an acidic medium. This can be considered as a batch operation system step.
7. Final concentrated solution of chrome(III) is poured into another tank for final basicity adjustment (33°Sch). In addition, this chrome (III) solution can be used back to the tanning industrial process.

Economical cost are also analized; meanwhile, it should be kept in mind that the resin can be reused several times, (up to 40 recycles); therefore, total cost of the investment will be lowered. This alternative new process allows to treat any chrome (III) effluent, even highly masked ones (acetate, formate, etc).

In this part of the work, the wastewater chromium concentration obtained by the reduction taken place in a batch operation, washing and rinsing stage, are determined.
2.8.3. CHROMIUM RECOVERY.

The chromium recovered in the ionic exchange process is influenced directly by the method used in the reduction-elution stage. The chromium quantity recovered is bigger when the reduction is achieved in-situ. The chromium recovered as determined in percentages uses the following equation:

\[
\text{Recovery ratio} = \left( \frac{\text{Cr}_{\text{eluted}} + \text{Cr}_{\text{columns}}}{\text{Cr}_{\text{loaded}}} \right) \times 100
\]

In Table 3, the experimental result obtained using hydrogen peroxide as reducer are presented; at the same time, shows the chromium recovered once the ionic exchange process have been carried out.

**Tabla 3 : Chromium recovered using hydrogen peroxide as reducer.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr loaded (mg)</th>
<th>Cr recovered (mg)</th>
<th>Recovered ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM1</td>
<td>2035</td>
<td>1733</td>
<td>85</td>
</tr>
<tr>
<td>SAM2</td>
<td>2131</td>
<td>1706</td>
<td>80</td>
</tr>
<tr>
<td>SAM3</td>
<td>1749</td>
<td>1601</td>
<td>92</td>
</tr>
<tr>
<td>SAM4</td>
<td>1792</td>
<td>1659</td>
<td>93</td>
</tr>
<tr>
<td>SAM5</td>
<td>2013</td>
<td>1776</td>
<td>88</td>
</tr>
</tbody>
</table>

**Figure 5 : Chromium recovered through Ionic Exchange (reducer hydrogen peroxide).**

In Table 4, the experimental results obtained using sodium disulfite as reducer are presented. At the same time, Figure 6, displays the recovered chromium once the ionic exchange process have been carried out.
Tabla 4: Chromium recovered using sodium disulfite as reducer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr loaded (mg)</th>
<th>Cr recovered (mg)</th>
<th>Recovered ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM6</td>
<td>1815</td>
<td>1323</td>
<td>73</td>
</tr>
<tr>
<td>SAM7</td>
<td>2044</td>
<td>1436</td>
<td>70</td>
</tr>
<tr>
<td>SAM8</td>
<td>1985</td>
<td>1484</td>
<td>75</td>
</tr>
<tr>
<td>SAM9</td>
<td>1750</td>
<td>1187</td>
<td>68</td>
</tr>
<tr>
<td>SAM10</td>
<td>1855</td>
<td>1458</td>
<td>79</td>
</tr>
</tbody>
</table>

Finally, Table 5 presents the experimental results obtained using glucose as reducer agent. In a similar way Figure 7 shows the chromium recovered once the ionic exchange process has been performed.

All the experiences have been achieved over the same conditions using in every time a new resin. In the first cycles, the resin retains certain quantity of chromium, but after several cycles, the retention is minimum. Therefore, the chromium recovered is even better.

Figure 6: Chromium recovered through Ionic Exchange (reducer sodium disulfite).

Tabla 5: Chromium recovered using glucose as reducer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr loaded (mg)</th>
<th>Cr recovered (mg)</th>
<th>Recovered ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM11</td>
<td>1712</td>
<td>1205</td>
<td>70</td>
</tr>
<tr>
<td>SAM12</td>
<td>1926</td>
<td>1300</td>
<td>67</td>
</tr>
<tr>
<td>SAM13</td>
<td>1893</td>
<td>1225</td>
<td>65</td>
</tr>
<tr>
<td>SAM14</td>
<td>2176</td>
<td>1551</td>
<td>71</td>
</tr>
<tr>
<td>SAM15</td>
<td>1932</td>
<td>1423</td>
<td>74</td>
</tr>
</tbody>
</table>
2.9. SCHEME OF THE ORIGINAL PROCESS.

Figure 7: Chromium recovered through Ionic Exchange (reducer glucose).

Figure 8: Scheme of the original process.
**Figure 8** shows that the resin is not removed from the column at any time. The reduction reaction is generated entirely inside the column. As a result of the reaction we obtain a liquor rich in Cr\(^{3+}\) ready to tan and a liquid residue that will be sent to treatment.

### 2.10. SCHEME OF THE MODIFIED PROCESS.

As a final result, we obtain the same products as in the case show previously. Now, however, these final products are obtained from the bottom of the sleeved reactor. In this new reduction system the visual control of the reaction is total, and this makes it possible to decide without any problem when the reaction has ended.

Loading the resin in the column, once the Cr\(^{3+}\) had been reduced and recovered Cr\(^{3+}\), was done manually. This operation is done in this way for the sake of the operation’s greater simplicity, although it could be carried out in an automatized manner without any inconvenience. **Figure 9** shows how the new system is employed to reduce dichromate to Cr\(^{3+}\). The resin is removed from the interior of the column via fluidization and later reduced in a sleeved reactor.

### 3. CONCLUSIONS

1.- Contribution to set up an alternative process to recover tannery- chrome (III) effluents, different to the conventional precipitation one. This process is based on the oxidation of chromium (III) to chromium (VI), followed by two sequential steps: a) fixation into an ion-exchange resin and, b) reduction to chromium (III) in a batch combined system.

2.- Several oxidation methods have been assayed, in order to improve the final results obtained with hydrogen peroxide. In spite of this, an oxidation with air could be a previous stage to the hydrogen peroxide in order to oxidize part of the organic matter present in the sample.
3.- The oxidation reaction of chromium (III) to chromium (VI) takes place by the action of hydrogen peroxide in an alkaline medium; such as: sodium carbonate, which has proved to be the best.

4.- In different experiences, both laboratory level and Pilot –Plant scale, the outlet of the column has given non detectable chromium eluent (less than 0.5 ppm).

5.- In the reduction stage, it has been used three different kinds of reducing agents; such as: hydrogen peroxide, sodium disulfite and glucose; the first being far the best. It is important to mention that this operation is a completely a novelty respect the previous process, which the reduction took place “in situ”, inside the column; nevertheless, in this new process the ion-exchange resin-dichromate bound is conveyed to a reactor vessel, where the reduction will undergo with better temperature control. At the end of the reduction, washes, etc, the resin will be adjusted to a proper pH and poured into the column to start a new cycle.

6.- Concerning to the chromium recovered, according to the results obtained, it can be seen that using the different reducing agents an excellent chromium recovered ratio has been achieved; emphasizing the chromium recovered using hydrogen peroxide has reached up to around 97% of recovery.

7.- The recovered concentrated solution of chromium (III) was basified to 33° Sch of basicity, with addition of sodium sulphate, then the liquor could be used into the traditional tanning operation. This recovered basified chromium (III) liquor produces a clear, uniform light blue colour in all grain surface; thus allowing to finish the leather in all range of light colours.

8.- A thorough economical study is ongoing, in order to compare the cost of both processes; a) precipitacion with magnesium and/or calcium oxides, and b) with the present new proposal. It is fundamental to underline that the ion-exchange commercial resin can be recycled, at least 40 times; therefore, diminishing significantly the cost of this product and the whole process.

4. BIBLIOGRAPHY.

1.- Yasuda, Sinichi; “Recovery of Chromium (VI) in wastewater”, 1979, Kokai Tokio, 14, 396.
18.- Young, H.; US Patent n°3,950,131, solicited at 13/03/76, “Continuous Method for Reclaiming Chromium Hydroxide from Spent Tanning Liquors and Re-use Thereof in Subsequent Tanning”.
5. ANNEX
5.1. PROVENANCE OF THE WATERS
Residual waters from the ECCO Leather B.V. company based in Dongen (Netherlands) were also used. Their main characteristics are:

- pH: 3.71
- Chromium: 0.35%
- Formiate: 936.4 mg/l
- Chloride: 12,892 mg/l
- Sulfate: 23,032 mg/l

5.2. PROCESS DIAGRAM.
The steps in the process used to carry out the pilot plant scale testing are shown in Figure 10. These steps are described in detail in the sections that follow.

Figure 10 - General process diagram, with in-reactor reduction.
Figure 11. General Process Diagram