



## Obtaining sodium chromate from ash produced by thermal treatment of leather wastes

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### ABSTRACT

Currently, 80–90% of leather production uses chromium tanning; thus, the trimmings and shavings resulting from the manufacturing of leather goods create a waste with a high pollution potential. One alternative for handling this scrap-leather waste is thermal treatment (gasification and combustion). The ashes generated during this process are rich in chromium, containing between 50% and 60% chromium oxide ( $\text{Cr}_2\text{O}_3$ ) by mass, and the ashes can thus potentially be utilized as a source of chromium for the synthesis of sodium chromate ( $\text{Na}_2\text{CrO}_4$ ). With the aim of improving on the results of previous attempts made to recover chromium from these ashes, in this work, the use of sodium nitrate to oxidize the trivalent chromium to the hexavalent form was studied. The resulting conversion of chromium (III) to chromium (VI) achieved was over 94%, and the sodium chromate obtained from the ashes showed physical properties similar to the commercial product.

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### 1. Introduction

Sodium chromate is a yellow solid, very soluble in water, and a strong oxidizing agent. It is a basic intermediate chemical product, from which all the other chromium compounds are produced [1,2]. Currently, there are over 70 chromium compounds in commercial use. However, only a few of these compounds are produced in large quantities, notably sodium chromate and dichromate, potassium chromate and dichromate, chromic acid, chromic oxide and basic chromic sulfate [3].

The traditional process for the production of sodium chromate consists of three procedures: the roasting of chromite ore, water leaching and multi-stage evaporation and crystallization [4].

During the industrial production of sodium chromate, the mineral chromite is used as a raw material. Chromite is a solid mixture of  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ ,  $\text{FeO}\cdot\text{CrO}_3$ ,  $\text{MgO}\cdot\text{CrO}_3$  and  $\text{MgO}\cdot\text{Fe}_2\text{O}_3$  spinels. This mineral contains between 40% and 50% chromium oxide ( $\text{Cr}_2\text{O}_3$ ). The method commonly used for the oxidation of chromium (III) to chromium (VI) is the utilization of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and dolomite or calcium oxide at high temperature, between 1200 and 1400 °C, in an oxidizing atmosphere [1,4,5]. The dolomite and the calcium oxide are used to avoid agglomeration of chromite parti-

cles and to enhance the diffusion of oxygen throughout the reaction mixture.

The traditional process of sodium chromate production results in a large amount of waste containing chromium [1,4,6]. In the United States, chromate production has generated millions of tons of waste; in the area of Baltimore alone, for example, more than 2 million tons of chromium-containing wastes have been deposited in landfills [7]. In some cases, up to 4 tons of “chromic mud” per ton of product is created [1]. Hence, several researchers have addressed their efforts toward developing new technologies for sodium chromate production, toward finding alternative sources of chromium oxide, such as reutilization and recycling of wastes, and for the treatment of wastes containing chromium (III) and (VI) [1,2,3,6,16–19]. To this end, a number of researchers have investigated chemical alternatives for the oxidation of chromium (III) using numerous chemical compounds and their combinations at different temperatures and conditions [4,5,8–11]. One alternative source of chromic oxide is the ash obtained by the thermal treatment (gasification and combustion) of leather wastes from the footwear industry.

The production of leather and leather footwear generates wastes classified as hazardous because of the presence of chromium, which is used in leather tanning; hence, these wastes require an appropriate treatment prior to disposal.

Different alternatives for the treatment of scrap-leather waste have been studied, among them thermal treatment (gasification and or combustion) [12,13]. The ashes generated during the process contain between 50% and 60% chromium oxide by weight.

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**Table 1**  
Chemical composition of chromite and ash.

Compound or element	Chromite (%)	Ash (%)
Cr <sub>2</sub> O <sub>3</sub>	51.18	55.91
Fe <sub>total</sub>	12.52	2.59
SiO <sub>2</sub>	4.68	23.58
Al <sub>2</sub> O <sub>3</sub>	11.59	7.35
CaO	2.95	1.20
MgO	12.11	–
Fe <sub>2</sub> O <sub>3</sub>	7.97	2.59
P	0.01	1.59
S	0.09	2.81
Cl	–	0.72
K <sub>2</sub> O	–	0.79
TiO <sub>2</sub>	–	1.53
Na <sub>2</sub> O	–	1.08

They can thus potentially be utilized as a raw material to produce sodium chromate, which is the precursor of basic chromium sulfate, the salt widely used in the tanning process. Comparing the composition of chromite and the composition of the ashes, it was observed that both have similar concentrations of chromium oxide; thus, the ashes could likely be used as a substitute for a natural chromium source. The detailed composition of chromite [14] and ashes obtained from thermal treatment of leather wastes is shown in Table 1. Ash composition was obtained by X-ray fluorescence spectrometry [13].

In previous studies, the industrial process conditions were considered by submitting the ashes generated during the thermal treatment to alkaline fusion with sodium carbonate at a temperature of ~1200 °C [10]. The investigated variables were influenced by process temperature, reaction time and heating rate. According to the results obtained, the optimum conditions for sodium chromate production from footwear wastes were a temperature of 1180 °C and a heating rate of 8 °C/min; the chromium-oxidation was 99.5% [10].

Pereira used an excess of sodium hydroxide (NaOH) for the oxidation of chromium (III) to chromium (VI), and the reaction temperature was reduced to 700 °C [5]. The influences of temperature, reaction time and air flow on the formation of sodium chromate were analyzed, where the process of chromium-oxidation was the main goal. At the end of the oxidative process, the excess of NaOH was extracted with a methanol solution. The sodium chromate was the recovered for 22.5 min under the optimal temperature of 700 °C and air flow of 75 L/h. The conversion of trivalent to hexavalent chromium was estimated to be approximately 83%.

In this work, the utilization of sodium nitrate in a trivalent-to-hexavalent chromium-oxidation process was studied. The sodium chromate obtained was considered an attractive source of basic chromium sulfate, which can be further used in hide tanning.

## 2. Materials and methods

### 2.1. Materials

The ashes utilized in this work were obtained from a thermal-treatment pilot plant for leather wastes. The ashes were collected in ashtrays of the gasification reactor, ground to particle sizes less than 75 μm and stored in appropriate bottles until further use.

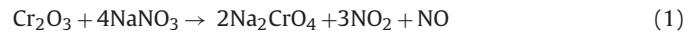
The chromium oxide concentration was determined (as chromium (VI)) according to the methods specified by the American Society for Testing and Materials – ASTM D-2807-93 (1998) [15]. The obtained results were confirmed by applying atomic-absorption analysis. The analysis of chromium (VI) content in the ashes showed that, for the purposes of this work, the quantity of chromium (VI) was negligible (less than 400 mg/kg) [13].

**Table 2**  
Variation of mass and molar ratios.

Excess of reagent NaNO <sub>3</sub> (%)	Molar ratio Cr <sub>2</sub> O <sub>3</sub> /NaNO <sub>3</sub> (mol/mol)	Mass ratio NaNO <sub>3</sub> /ashes (R; g/g)
0	1/4	1.10
50	1/6	1.65
100	1/8	2.20
200	1/12	3.30
400	1/20	5.50

### 2.2. Sodium chromate production

The stoichiometry of the reaction between sodium nitrate and chromium oxide can be written as follows:



The reaction between the reactant mixture, the melted material and the ashes was carried out in a cylindrical crucible with a high alumina content. The mass ratio of sodium nitrate to ashes,  $R$  (g/g) and the corresponding excess of reagent are shown in Table 2.

The heating process was performed at a rate of 10 °C/min until the desired reaction temperature,  $T$  (°C), was reached. The cylindrical crucible containing the mixture was put in a heating furnace (Fig. 1) with temperature control. The air was fed into the mixture through a high-alumina tube inserted into the center of the crucible. The air flow,  $V$  (L/h), was controlled with a rotameter.

At the end of the reaction time,  $t$  (min), the crucible was transferred to an oven at temperature of ~200 °C for a gradual crucible cooling.

At these conditions, the mixture was leached due to the high solubility of sodium chromate. The solution obtained was filtered using a glass-fiber filter with a Büchner funnel. The cake was leached with water at room temperature until the water ran clear and colorless, that is, without the characteristic bright yellow color of sodium chromate.

The influences of process temperature, mass ratio ( $R$ ), air flow and reaction time of the chromium-oxidation were investigated. All the experiments were performed in duplicate.

The melting point of sodium nitrate is 308 °C [9]; thus, the experiments were performed at higher temperatures in order to ensure the molten state of the reaction mixture. The goal of air introduction was to promote the chromium-oxidation reaction.

The degree of chromium-oxidation,  $u$  (%), was calculated as follows:

$$u (\%) = \left( 1 - \frac{Cr_f}{Cr_i} \right) * 100 \quad (2)$$

where  $[Cr_f]$  is the final fraction of chromium oxide in the residue (filter) and  $[Cr_i]$  is the initial fraction of chromium oxide in the ashes.

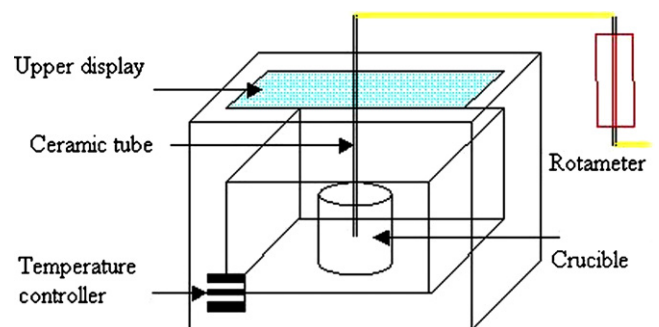


Fig. 1. Heating furnace.

**Table 3**  
Results of chromium-oxidation in leather ashes.

Exp.	T (°C)	V (L/h)	R (g/g)	t (min)	u (%)
1	500	0	3.3	90	1.70
2	600	0	3.3	90	10.93
3	700	0	3.3	90	77.44
4	750	0	3.3	90	94.33
5	800	0	3.3	90	91.70
6	900	0	3.3	90	87.37
7	750	50	3.3	90	94.11
8	750	100	3.3	90	94.63
9	750	0	1.1	90	53.43
10	750	0	1.65	90	86.50
11	750	0	2.2	90	95.50
12	750	0	5.5	90	95.00
13	750	0	2.2	0	11.89
14	750	0	2.2	30	82.50
15	750	0	2.2	60	94.00
16	750	0	2.2	90	95.50
17	750	0	2.2	120	94.00

The concentrations  $[Cr_i]$  and  $[Cr_f]$  were determined according to ASTM D 2807 – 93 (1998) [15]. These results were compared with those obtained by atomic-absorption analysis, and we concluded that the two analytical techniques gave similar results.

### 2.3. Characterization of sodium chromate

Sodium chromates obtained in the laboratory and the commercial product were both characterized by scanning electron microscopy (SEM) and X-ray diffraction analyses.

### 2.4. Analysis of residues generated during sodium chromate production

The chromium fraction in the residue was analyzed according to the method given in ASTM D 2807-93 (1998) [15]. The residues were also analyzed by X-ray diffraction and X-ray fluorescence analytical methods.

## 3. Results and discussion

### 3.1. Recovery of sodium chromate

The results obtained from the oxidation of chromium in the ashes showed that, at a reactant mass ratio of 3.3 and a reaction time of 90 min without air flow, increasing the process temperature beyond 750 °C caused no increase in oxidation (Table 3, Exps. 1–6). A satisfactory conversion value was obtained at 750 °C reaction temperature (94.33%). At higher reaction temperatures (800 and 900 °C), the oxidation yields decreased. This may be because at these temperatures sodium nitrate decomposes rapidly (sodium nitrate decomposition began at ~600 °C).

Addition of air to the reaction mixture did not increase the chromium (III) to chromium (VI) conversion. For an air flow of 50 L/h, the oxidation was 94.11%, and when the air flow was doubled to 100 L/h, the oxidation did not increase (94.63%). An increase in the mass ratio  $R$  would likely be assumed to have a positive effect on the chromium-oxidation process, but an increase was not observed for the ratios over 2.2.

For a 60-min reaction time, the conversion was 94%, and further increasing the reaction time did not affect the conversion value.

### 3.2. Characterization of sodium chromate

The properties of the product obtained from the ashes were compared with those of the commercial product using scanning electron microscopy (SEM) and X-ray diffraction analyses.

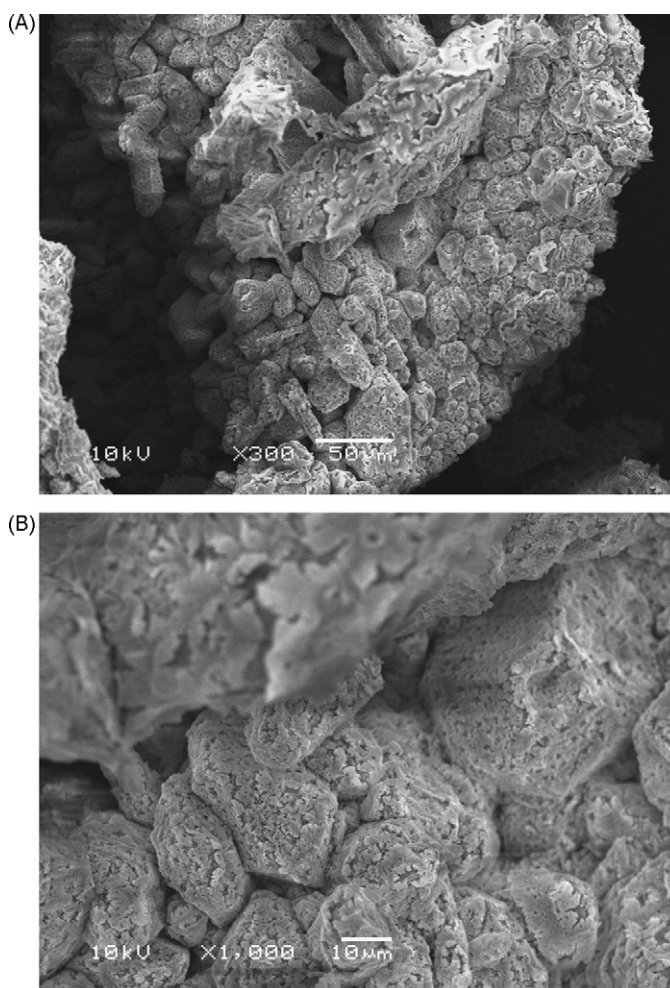
Figs. 2 and 3 show electron micrographs of the surfaces of commercial sodium chromate and that obtained in our experiments, respectively.

The surfaces of these materials were assumed to be different due to their different methods of production. It should be noted that the commercial product was obtained from chromite ore; thus, the reactants used to obtain industrial sodium chromate were different from those used in this work, and the process conditions differed as well. The industrial process utilized higher temperatures, ~1200 °C, while the reaction in the laboratory was carried out at ~750 °C.

Figs. 4 and 5 show the X-ray diffraction analyses of the commercial sodium chromate and the one obtained in the laboratory. In both samples, the same compounds were identified. Hence, although different chemical processes were used for their syntheses, the final products showed similar compositions.

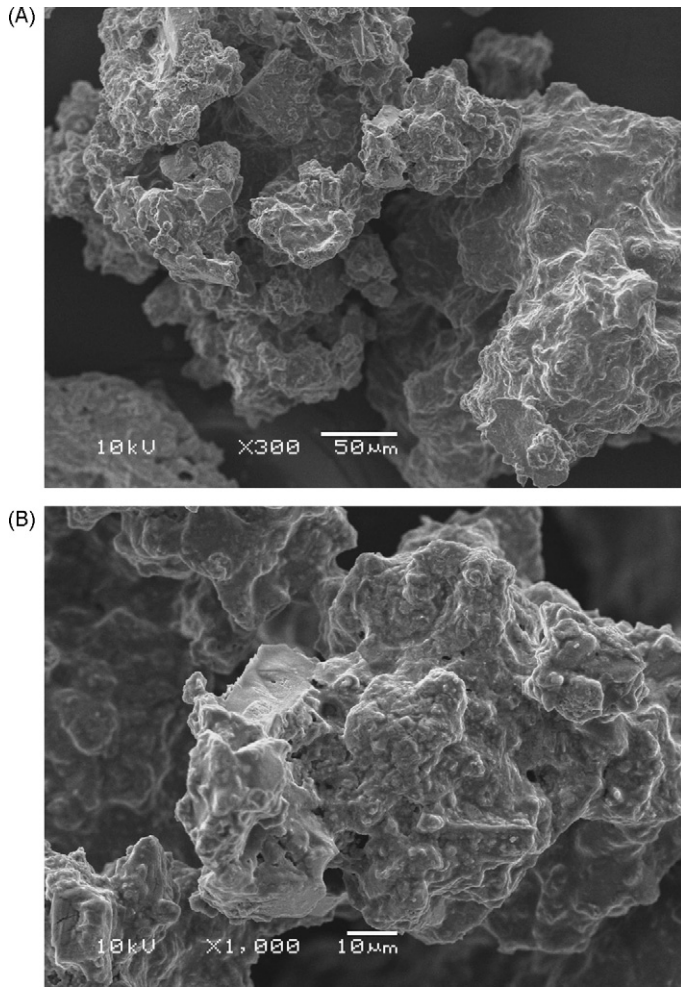
### 3.3. Analysis of wastes

Analyses of the non-oxidized chromium on the filter, unreacted sodium nitrate and other compounds of the ashes were performed. The result of the X-ray diffraction analysis of the filter residue is shown in Fig. 6; compounds of silicon, aluminum, pyrite (ferrous compound), chromium and sodium were detected. The last two compounds were from the incomplete oxidation of chromium present in the ashes and the excess of sodium nitrate used in the oxidation reaction.



**Fig. 2.** SEM of commercial sodium chromate: (a) 300× magnification, (b) 1000× magnification.

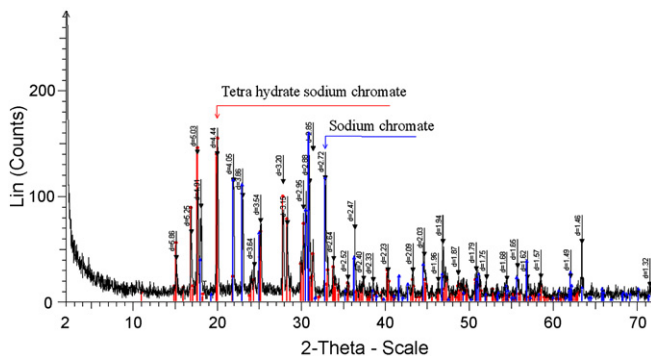




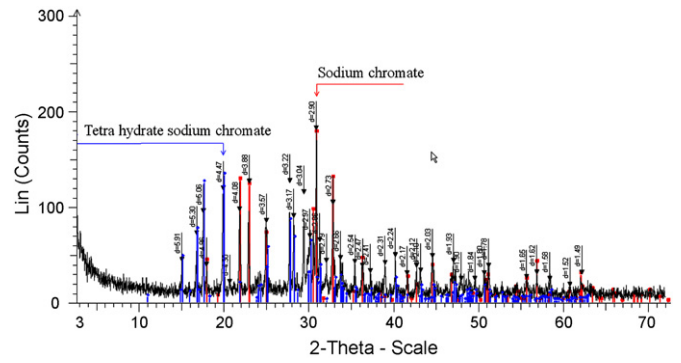
**Fig. 3.** SEM of sodium chromate obtained in the laboratory: (a) 300× magnification, (b) 1000× magnification.

The major compounds detected in the filter residue by X-ray fluorescence are shown in Table 4.

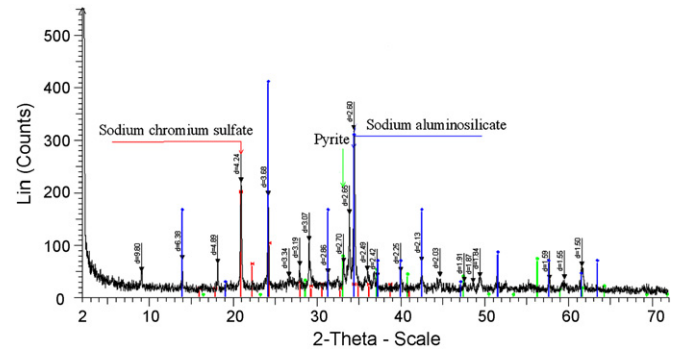
The most common compounds in the residue were silicon, aluminum, iron, chromium and sodium, which were the same as those detected by the X-ray diffraction technique. The chromium oxide percentage in these samples was similar to the one detected by the ASTM D 2807-93 (1998) [15] method, about 3%. An increase in the amount of sodium in the residue was observed in comparison with the results obtained by Godinho et al. [13], who detected about 1.08% sodium oxide in the ashes before the chromium recovery. This increase can be considered to be a consequence of the excess



**Fig. 4.** X-ray diffraction analysis of the commercial sodium chromate.



**Fig. 5.** X-ray diffraction analysis of sodium chromate obtained in the laboratory.



**Fig. 6.** X-ray diffraction analysis of filter residues.

sodium nitrate used during the chromium-oxidation reaction. The relative increase of other compounds can be explained due to the decrease in the amount of chromium.

### 3.4. Economical and environmental analysis

An economic analysis (data not show) for the production of basic chromium sulfate, salt widely used in leather tanning was made. This study was based on work developed by Pereira [5] and used as raw material sodium chromate obtained from the ashes of the thermal treatment of leather waste, via oxidation with sodium hydroxide. It follows that for an annual production of 9.3 thousand tonnes of basic chromium sulfate would require an initial investment of \$ 2.6 million, and the time for return on invested capital would be approximately 5 years also the final product would be sold at 50% of market value of commercial product. Thus, it is possible to estimate that the route proposed in this paper is also economically advantageous because it uses sodium nitrate, material cheaper than sodium hydroxide and using similar reaction conditions.

**Table 4**  
Composition of filter residue.

Chemical compounds and groups	%
Cr <sub>2</sub> O <sub>3</sub>	2.64
SiO <sub>2</sub>	31.72
Al <sub>2</sub> O <sub>3</sub>	13.81
TiO <sub>2</sub>	2.75
Fe <sub>2</sub> O <sub>3</sub>	10.46
MnO	0.06
MgO	1.80
CaO	4.17
Na <sub>2</sub> O	25.54
K <sub>2</sub> O	0.1
P <sub>2</sub> O <sub>5</sub>	0.13
SO <sub>4</sub>	1.28

Through analysis of the mass remaining in the filter used in this work, it was observed that remained approximately 18.26% of the initial total mass (ash + sodium nitrate). In this process, depending on the oxidation obtained for chromium, it is estimated that for every ton of sodium chromate produced is generated 0.61 tons of waste. So, this route produces less waste than the routes commonly used today, which generate large quantities of waste. In some cases, up to 4 tons of “chromic mud” per ton of product is created [1].

#### 4. Conclusions

The results indicate that obtaining sodium chromate from the ash resulting from the thermal treatment of leather waste is a viable alternative to the commercial product. The reaction temperature significantly influenced the oxidation of trivalent chromium and in this work was markedly lower than that used in the industrial oxidation reaction. The addition of air into the reaction mixture did not increase chromium (III) conversion. In order to obtain satisfactory conversion, it was necessary to use an excess of molten sodium nitrate. However, reaction times over 60 min did not increase chromium-oxidation conversion.

Surface differences between the commercial and laboratory products were observed, while the X-ray diffraction analysis showed that the products had similar compositions.

In the filter residues, the contents of chromium, sodium, silicon, aluminum, ferrous and other oxides were also identified by X-ray fluorescence spectroscopy.

Sodium nitrate can be considered to be a good oxidizing flux material for the process of trivalent chromium-oxidation, and the alternative of recovering chromium from leather-waste ashes is very economically and environmentally attractive, which should promote further industrial development of the process.

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