

# INFLUENCE OF TEMPERATURE AND HOLDING TIME ON HEXAVALENT CHROMIUM FORMATION DURING LEATHER COMBUSTION

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## Summary

Previous studies indicated that Cr(VI) was not detected or was below 5 mg/kg in tanned leather scraps. However, after they are burned, the resulting ashes contain meaningful amounts of Cr(VI) that depend on the burning temperature. Furthermore, results obtained at the same ignition temperature, but different holding times, show high variability.<sup>1-3</sup>

This paper presents experimental results that confirm the Cr(III) to Cr(VI) transformation during chromium tanned leather combustion and its dependence on temperature and time, thus finding an explanation for variability of the results published before.

## Introduction

Chromium is a trace element found in the Earth's crust and in ore deposits exists mainly as  $\text{FeCr}_2\text{O}_4$ . In the environment, chromium is usually found in the trivalent state and less frequently in the hexavalent state, these two oxidation states having different toxicity and mobility.<sup>4</sup> Trivalent chromium, Cr(III), is an essential nutrient for humans, being relatively non-reactive and immobile.<sup>5</sup> Contrarily, hexavalent chromium, Cr(VI), is classified as a human carcinogen, being rather mobile.

Chromium is used in many industrial applications, namely in leather tanning. Leather scrap is a waste management problem for the leather, footwear and allied industries due to the high quantities and volumes of these residues that they generate.

Leather's high calorific value makes its use as a heat source logical and justifies some experimental effort in order to determine contaminants and their levels, the released gases and as well, to monitor chromium and its oxidation state during the process. In fact, since there is a significant difference in toxicity between Cr(III) and Cr(VI), it is necessary to quantitatively differentiate between these two states in the solid state due to the correspondingly different waste management responsibilities. Several approved analytical methods exist for quantitative differentiation between Cr(III) and Cr(VI) in aqueous solutions, for the measurement of total chromium in solid phases and for the extraction of Cr(VI) from solid wastes.<sup>1-4,6-10</sup>

Previous research was carried out with the following objectives:

- (i) select the method that gives the best results for extracting and analysing total Cr(VI) in leather solid wastes and leather combustion ashes, promoting no Cr(III) oxidation or Cr(VI) reduction during the analysis<sup>1</sup>; and
- (ii) study Cr(III) oxidation during combustion of chromium tanned leather residues.<sup>2,3</sup>

Preliminary results indicate that, in the leather wastes, Cr(VI) is leached at a level less than 5 mg/kg of leather. However, when wastes are burned, the resulting leather ashes contain appreciable Cr(VI) amounts that depend

on the burning temperature. These results showed high variability.<sup>1-3</sup>

This paper confirms that Cr(VI) formation is dependent on leather combustion temperature as well as holding time of the ashes, and is a part of research having as its objective, the study of Cr(III) to Cr(VI) transformation during chromium leather combustion.

## Experimental

### Materials and equipment

The reagents and materials used in this present work were: chemicals of analytical grade; double distilled water; 33% basic chromium sulphate; chromium tanned leather currently used in footwear applications with the characteristics presented in Table I and tanned using the above tanning agent (TA). A Frisch Pulverisette cutter mill, type 15.103, with knives rotating at 700–1000 rpm and a sieve of 4 mm diameter mesh; quartz crucibles and dishes; electric furnace (Heraeus, type M 110) calibrated over the range of 300–1000°C; UV-VIS spectrophotometer (Perkin Elmer, Lambda 2); pH analyser (Metrohm 691); and, centrifuge (Heraeus, Megafuge 1.0).

TABLE I  
Characteristics of the leather used

Parameter	Standard	Unit	Result
Thickness	UL.F.0006A.00	mm	2.30
Tear strength	BS 3144.6	N	//223.2; $\perp$ 179.2
Tensile strength	BS 3144.5	MPa	//14.5; $\perp$ 23.6
Elongation at break	BS 3144.5	%	//62.0; $\perp$ 55.6
Substances soluble in dichloromethane	BS 1309	%	16.1
Chromic oxide	BS 1309	%	3.8
Sulphate total ash	BS 1309	%	4.0
Sulphate water-insoluble ash	BS 1309	%	0.4
pH value	BS 1309	%	3.6
Difference figure of an aqueous extract	BS 1309	%	0.5

// = parallel samples.

$\perp$  = perpendicular samples.

### Methods and procedure

In our previous work, methods for leaching Cr(VI) from leather and leather ash samples used aliquot amounts of all the reagents proposed by US EPA EP Toxicity Leaching Procedure (EPTox), US EPA Toxicity Characteristic Leaching Procedure (TCLP), a deionised water neutral protocol and a phosphate buffer protocol. TCLP gave the most environmentally conservative results and was therefore selected as the leaching procedure to be used in the research.<sup>1,2</sup> Also, taking into account the literature survey performed and our previous work, the US EPA SW-846 Method 7196 (diphenylcarbazide reaction, pH 2, 540 nm spectrophotometer/colourimetric analysis) was selected to quantify the leached Cr(VI).<sup>1,2,11-14</sup>

### Sampling and ashing procedures

Four half hides were ground with the cutter mill, homogenised and stored in large bags. Prior to tests, samples were collected and conditioned at  $20 \pm 2^\circ\text{C}$  during 24 hours in an atmosphere with relative humidity of  $65 \pm 2\%$ .

In order to study the influence of the temperature cycle on the Cr(VI) leaching TCLP results, several experimental tests were carried out using dehydrated leather held at  $102 \pm 2^\circ\text{C}$  for 5 hours, as follows:

**Test A:** Several samples of both the ground leather and the basic chromium sulphate were held at temperatures in the range of  $300\text{--}1000^\circ\text{C}$  until constant weight. The total chromium in the samples, expressed as chromium oxide, was determined according to the BS 1309 recommended procedure and is reported in Table II.

#### Test B:

- 6 quartz crucibles with leather were loaded at the same time in an electric furnace and heated up to  $1000^\circ\text{C}$ ;
- One crucible was removed after the following holding periods at  $1000^\circ\text{C}$ : 30 min, 1 h 30 min, 2 h, 3 h, 4 h and 19 h.

#### Test C:

- A quartz capsule with leather was loaded in the electric furnace and heated up to  $1000^\circ\text{C}$ ;
- A sample of the previously homogenised ashes in the capsule was taken after the following holding periods at  $1000^\circ\text{C}$ : 30 min, 1 h, 1 h 30 min, 2 h 30 min, 3 h 30 min, 4 h, 5 h, 7 h and 24 h.

#### Test D:

- 8 quartz crucibles with leather were heated in the electric furnace up to  $300^\circ\text{C}$  and held for 2 h at this temperature, then all the crucibles were removed;

- The furnace was heated up to  $400^\circ\text{C}$ , then loaded with 7 crucibles that were held for 2 h at this temperature, and, again, one crucible was removed;
- This procedure was repeated at the temperatures of  $500, 600, 700, 800, 900$  and  $1000^\circ\text{C}$  with all but less one crucible, thus only the last one was heated at  $1000^\circ\text{C}$ .

#### Test E:

- A quartz capsule with leather was successively heated at the temperatures of  $300, 400, 500, 600, 700, 800, 900, 1000, 600, 400, 800, 600$  and  $1000^\circ\text{C}$  where it was held for 2 hours. After each temperature-time step a sample of ash was collected from the capsule.

The ashes were tested using TCLP and the obtained solution was analysed for Cr(VI) and this procedure was repeated at least twice, thus the reported results are the mean values.

## Results and Discussion

Table II shows, respectively, the total chromium content, as chromium oxide, and Cr(VI) leached from the samples obtained by heating chromium tanned leather and basic chromium sulphate tanning agent (TA) in the temperature range of  $300$  to  $1000^\circ\text{C}$ , until constant weight. Since the original leather and tanning agent leached no detectable Cr(VI), these *Test A* results indicate that heating cycles in the  $300\text{--}1000$  range increase the levels of Cr(VI) leached from the resultant products. Furthermore, the amount of Cr(VI) leached is temperature dependent, and the leather ashes show higher Cr(VI) levels for burning temperatures below  $500^\circ\text{C}$  and above  $800^\circ\text{C}$ .

Basic chromium sulphate shows a similar behaviour to that of the leather, despite the observed large difference at  $300^\circ\text{C}$  (in fact the value of  $130\text{ mg Cr(VI)/kg}$  of TA ash is the mean average of  $128$  and  $132\text{ mg Cr(VI)}$  and that of  $27477\text{ mg Cr(VI)/kg}$  of leather ash is the mean average of  $11235, 35050, 34946, 21826, 25595$  and  $36213\text{ mg Cr(VI)}$ ).

Fig. 1 expresses the Cr(VI) leached as a function of  $\text{Cr}_2\text{O}_3$  contained both in leather ashes and TA ashes at different temperatures. As shown, the quantity of Cr(VI) formed in the tanning agent is usually higher than in the tanned leather, mainly at temperatures above  $800^\circ\text{C}$ .

Fig. 2 depicts the results of the *Test B* and *C* experiments, where the main objective was to assess the influence of holding time on some of the heterogeneous results already obtained. The results corresponding to the same holding time, i.e., those at 30 min, 1 h, 1 h 30 min and 4 h are not equal. Nevertheless both tests show the same tendency of increasing Cr(VI) sample leachability with holding time up to a maximum around  $200\text{--}300$  minutes and then of the subsequent decrease. Thus, the time that the leather scrap is held at  $1000^\circ\text{C}$  has a strong effect on the hexavalent chromium that is leached from the ashes using the TCLP protocol. This effect can explain why some of the results of the Cr(VI) leached from *Test A* samples, corresponding to the same maximum heating temperature, had a standard deviation above  $10\%$  of its respective mean value. In fact these samples were burned till constant weight and the holding time was variable.

Fig. 3 shows the results from *Test D* and *E* experiments. They simulate different conditions of combustion and holding of the ashes, and gave us some help

TABLE II

Total chromium in leather ash and chromium sulphate heated in air at different temperatures to constant weight and Cr(VI) leached from *Test A* samples

Heating temperature, $^\circ\text{C}$	$\text{Cr}_2\text{O}_3$ , %		Cr(VI), mg/kg	
	Leather ash <sup>1</sup>	TA	Leather ash	TA
300	4.18	25.8	27477	130
400	4.17	25.5	27824	14042
500	4.09	28.0	4370	1401
600	4.13	30.3	575	1467
700	4.16	31.2	2527	883
800	4.13	31.4	4659	2654
900	4.09	36.9	10999	14181
1000	4.22	48.7	19028	33647

<sup>1</sup> Referred to the dry leather mass; TA = basic chromium sulphate tanning agent.

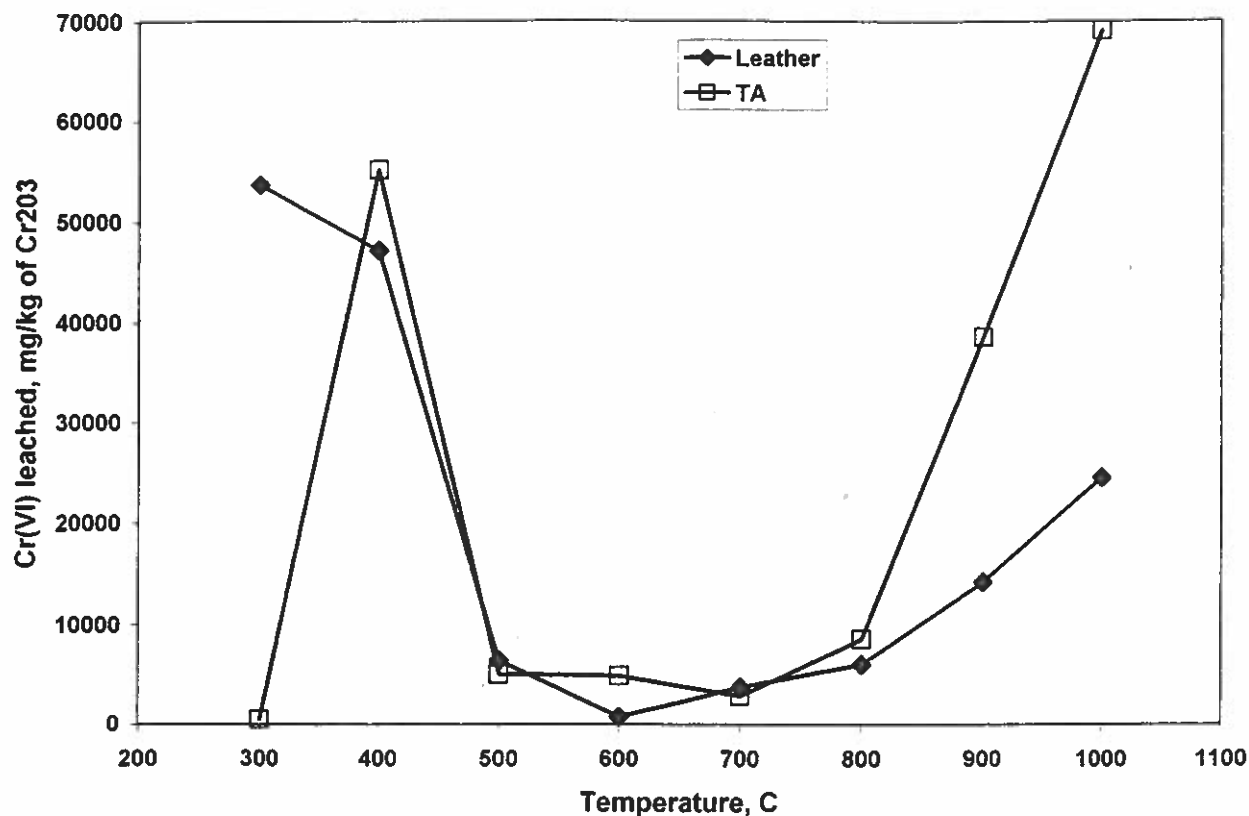


Figure 1. Cr(VI) leached from leather ashes and TA ashes heated at different temperatures.

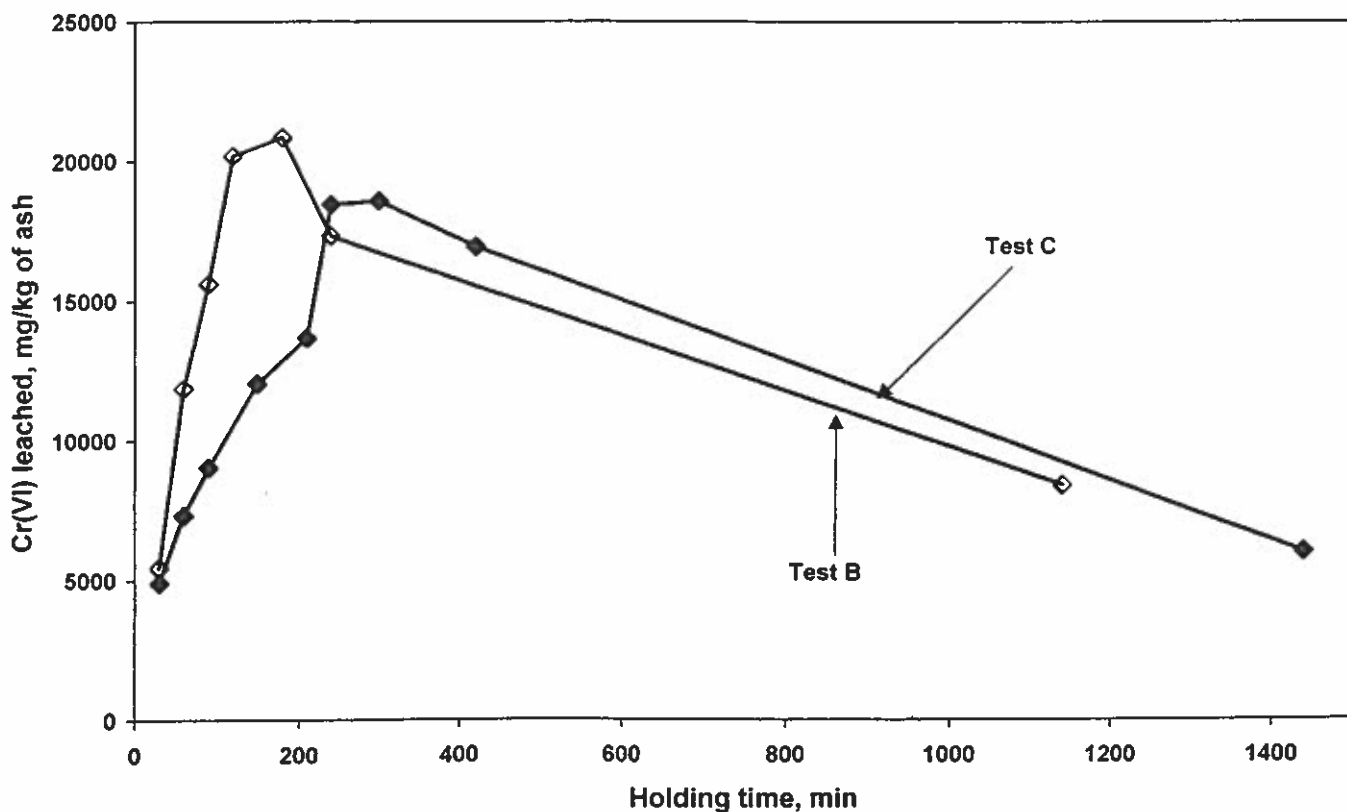


Figure 2. Cr(VI) leached from leather ashes as a function of holding time at 1000°C.

towards understanding why in the samples collected from two pilot combustion systems in development, Cr(VI) was leached less than expected by using the TCLP protocol (481 and 391 mg Cr(VI)/kg of ashes from fixed grate and fluidised bed furnaces, respectively).

The effect of successive ash heating followed by an

isothermal period confirms the higher Cr(VI) levels leached at temperatures below 600°C and above 800°C. Once 1000°C is reached, the amount of Cr(VI) leached from the ashes becomes practically constant when cooling them to 400°C but it can increase if they are heated again up to 1000°C.

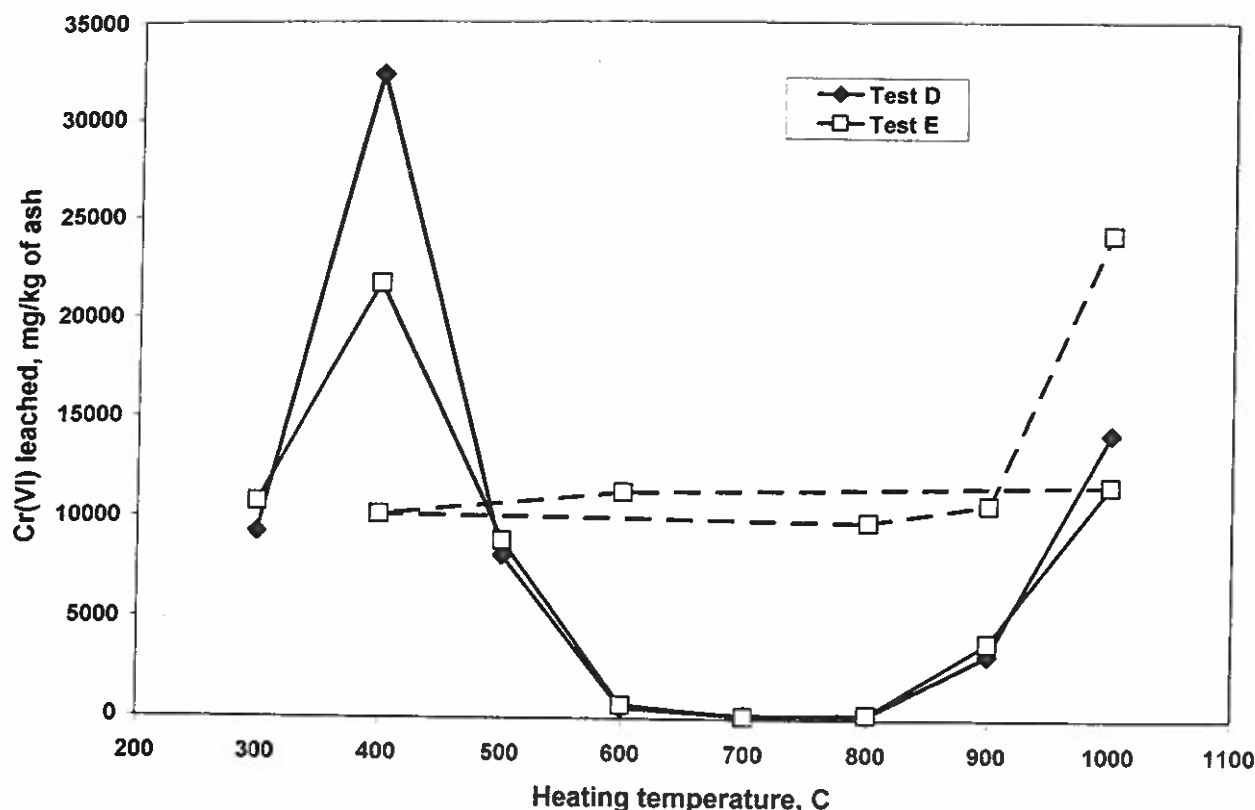


Figure 3. Cr(VI) leached from leather ashes submitted to successive thermal cycles.

## Conclusions

TCLP leaches Cr(VI) from the ashes produced by burning chromium tanned leather in the 300–1000°C range, in amounts largely exceeding the threshold value for this metal. Since Cr(VI) leached from both the chromium tanned leather and basic chromium sulphate is below the threshold value, it can be concluded that when leather scrap is burned in a normal air atmosphere it generates a hazardous waste that must be managed accordingly.

Nevertheless, Cr(VI) leaches from the leather ashes generally less than from the basic chromium sulphate submitted to the same temperature-time conditions. Therefore, it can be said that leather decreases Cr(VI) leachability, mainly at temperatures above 800°C.

The results show that Cr(VI) leached from the ashes using the TCLP method strongly depends on the burning temperature and holding time. The 600–800°C range is the less favourable to Cr(VI) leachability. Increasing holding time at certain temperatures may have an encapsulating effect over chromium contained in the ashes. These two effects allow for a possible explanation of the lower Cr(VI) leachability found for the ashes produced by the pilot systems under development, since in these furnaces combustion generally occurs over the broad temperature range of 600–800°C and ashes may remain in the furnace for a long time before discharge.

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