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USING ASHES FROM INCINERATION OF CHROMIUM SULPHATE TANNED LEATHER SCRAP PART 1: CHARACTERIZATION OF ASHES AND CHROMIUM EXTRACTION

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Summary

Chromium is the basis of leather manufacture and its extractable reserves are limited in distribution, mainly in South Africa, Zimbabwe and ex-USSR countries. Almost 20% of the metal is used by the chemical industry where one third of it goes into leather production as chromium sulphate tanning agent.[1] The European Union depends on chromium imports.

After burning leather scrap—tanned with chromium sulphate—the resulting very rich chromium ashes may present chromium (VI) in such a concentration that it becomes a hazardous waste and needs careful handling.[2,3]

Thus, both economic and environmental reasons suggest the use of these ashes. This paper mainly summarizes some of the conclusions of the research carried out during the execution of CRAFT project BRST-CT96-5085, where leather incineration ashes generated by two different pilot combustion systems, respectively a fixed grill incinerator (FGI) and a fluidized bed incinerator (FBI) were characterized and chromium was leached using a mixed pyrometallurgical and hydrometallurgical route as well as a full hydrometallurgical route.

Introduction

Nowadays, most of the leather used by footwear and leather goods manufacturers is tanned using trivalent chromium sulphate and the scrap generated is mainly dumped. In the few situations where incineration is used, mainly due to the leather's high calorific value in the range of 18 800–21 000 joules/g, the ashes obtained usually contain an appreciable amount of Cr(VI)—assumed to be carcinogenic—depending on the burning temperature and holding time.[2–4]

Generally no added value is given to these resulting ashes, despite the fact that they may contain 90–95% Cr_2O_3.

Trivalent chromium compounds are rarely soluble in water contrarily to the hexavalent ones whose formation is welcome from the point of view of some hydrometallurgical alternatives to recover the metal from the ashes. To the contrary, from other perspectives of using these leather ashes, it is practically imperative to have nil soluble chromium, even under action of very aggressive solutions and therefore almost no Cr(VI) compounds.

In such a scenario, thermal treatment of leather scrap must be justified not only by its high calorific value, but by taking into account as much as possible of the consequences of it, namely (i) pollutants and their levels in the released gases; (ii) characteristics of the ashes and factors that influence changes in the chromium oxidation state during the burning process as well as in some of the further ash treatment options. These considerations must be always directed to useful ends.

Among the alternatives for using leather ashes, one is as a chromium raw material from which metal is extracted into an aqueous solution, and for this purpose ashes may be either: (i) directly attacked by powerful acid oxidizing solutions such as those containing perchloric acid, or, (ii) mixed with alkaline fluxes, for example sodium carbonate, followed by a two-step process of heating and hot washing the fritt obtained.

Experimental Procedures

Methods and procedure

Chemical characterization of leather ashes considered in this study was obtained following BS 1309: 1974 and using X-ray fluorescence analysis (XRF), too, as reported in Table I. A Toxicity Characteristic Leaching Procedure (TCLP) was selected to verify leaching behaviour of both ashes and Cr(VI) in the leachate was determined using USEPA SW-846 Method 7196 (diphenylcarbazide reaction, pH 2, 540 nm spectrophotometer/colourimetric analysis).

The two sets of experiments in Table II followed the L4 matrix Taguchi design with 3 factors at 2 levels.[5] All the experiments were carried out in beakers with magnetic stirring and a constant solution volume:ash mass ratio of 25, i.e., 50 ml of solution and 2 g of FGI leather ashes. Sulphuric acid was added into the solution in the light of reaction (1), as the stoichiometric amount in two tests, as five times that amount in four experiments and as fifteen times the stoichiometric amount in the two other experiments. Two of the experiments in the first set were carried out with ashes previously ground. Similarly, the same procedure was followed with perchloric acid in the third set of

TABLE I
XRF results of the FGI and FBI ash analyses

Ash	Cr_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Na_2O	MgO	Al_2O_3	L.O.I.
FGI	51.8	14.7	–	4.5	4.7	0.5	<0.1	1.9	2.9	0.8	6.3	11.7
FBI	29.0	53.0	1.8	0.1	2.8	0.5	<0.1	0.7	1.8	0.5	1.9	5.2

L.O.I. = Loss on ignition.

TABLE II
Influence of acid concentration, grinding, temperature and time on chromium recovered from FGI ashes

No.	Set 1					Set 2				
	H_2SO_4	ground	T, °C	t, min	Cr, %	H_2SO_4	$HClO_4$	T, °C	t, min	Cr, %
1	5 stoic.	No	20	30	0.48	stoic.	stoic.	20	30	0.77
				90	0.68				90	0.82
				150	0.78				150	0.82
2	5 stoic.	Yes	90	30	0.97	stoic.	5 stoic.	90	30	1.64
				90	1.16				90	1.46
				150	1.45				150	1.73
3	15 stoic.	No	90	30	1.36	5 stoic.	stoic.	90	30	0.82
				90	1.74				90	0.86
				150	1.94				150	0.95
4	15 stoic.	Yes	20	30	1.45	5 stoic.	5 stoic.	20	30	2.19
				90	1.65				90	3.07
				150	2.04				150	4.41

experiments, the amounts added to the aqueous solution being calculated through reaction (2).

$$Cr_2O_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3H_2O \quad (1)$$

$$6ClO_4^- + 8Cr_2O_3 + 16H_2O \rightarrow 6Cl^- + 16HCrO_4^- + 16H^+ \quad (2)$$

All the experiments were followed by sampling the solution after 30, 90 and 150 minutes, then quantifying the chromium in the samples by atomic absorption spectrophotometry (AAS). The experiments at 90°C had periodic additions of deionized water in order to compensate for evaporation. Recoveries were computed by comparing total chromium in the 50 ml of solution with that calculated in the 2 g of ashes.

Fig. 1 refers to experiments also carried out using 0.2 g of ashes with the goal of optimizing the volume ratio of sulphuric and perchloric acids as well as the ratio between volume of mixture and mass of ashes. In these experiments beakers were heated at a high constant output of the heating plate for 30 minutes, but the temperature was not monitored.

The classic approach of recovering the chromium contained in the ashes can be viewed as based in reactions of type (3). Chromium is assumed as being in the form of Cr_2O_3 and made water soluble with the intervention of an oxidant and an alkaline metal as one or more of its salts added into the mixture, usually carbonate, hydroxide, nitrate and chlorate.

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2 \quad (3)$$

With this objective several 0.5 g samples were heated with either Na_2CO_3 or NaOH in small iron crucibles loaded in an electric furnace. The mass obtained was then leached with hot water and total chromium and silicon were determined in the solution by AAS, thus allowing us to calculate the percentage of these metals recovered. The experimental approach was first to determine the best reagent/ash ratio for several heating temperatures and then to look at the holding time influence.

In order to purify the ashes obtained by leaching as much as possible of its silica simultaneously with low chromium dissolution, a hydrometallurgical leaching route using sodium hydroxide solutions at a pressure higher than atmospheric in an autoclave was tested with FBI ashes.

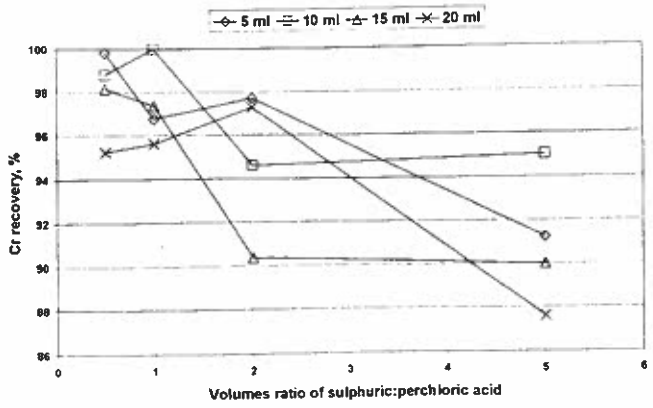

Figure 1. Chromium recovered from 0.2 g ash samples by hot sulphuric and perchloric acid mixtures as function of its total volume and acids ratio.

Results and Discussion

Characteristics of ashes

The Cr_2O_3 percentage in Table I obtained by XRF are not very different from those obtained through BS 1309: 1974 for FGI and FBI ashes, giving respectively: (i) 92.3 and 96.7% of ash content; (ii) 53.2 and 31.2% Cr_2O_3; and, (iii) pH of 9.2 and 9.5.

The Toxicity Characteristic Leaching Procedure (TCLP) gave 449.1 and 43.4 mg Cr(VI)/kg of ash leached from FGI and FBI ashes, respectively. Despite the fact that the dissolved chromium only represents 0.12 and 0.02% of total, respectively for FGI and FBI ashes, according to TCLP criteria both ashes are considered as hazardous wastes, since they largely exceed the chromium threshold value.

As shown, alkaline and alkaline-earth elements in FGI ashes occur in higher percentage than in FBI ashes.

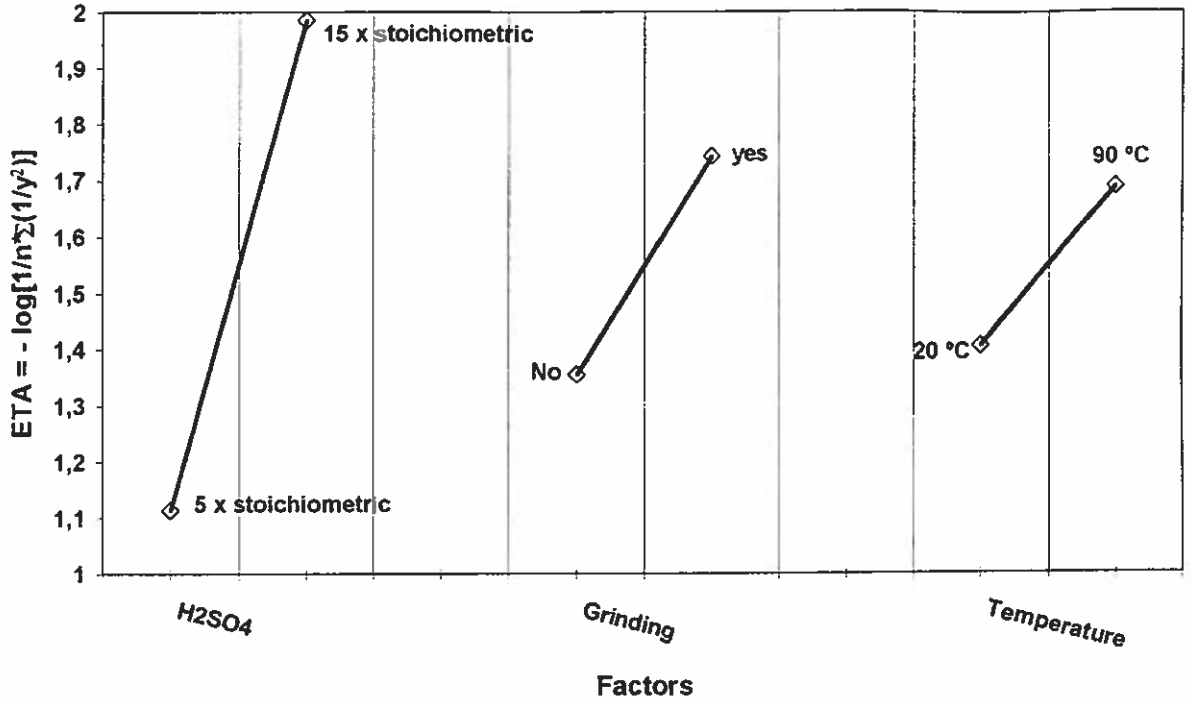

Figure 2. Influence of H_2SO_4 concentration, ash grinding and temperature on chromium recovered by leaching FGI ashes with sulphuric acid solutions at a liquid:solid ratio of 25.

On the contrary, silica in FBI ashes is much higher than in FGI ashes, as expected due to the sand-bed used. These two factors, i.e., lower amount of alkaline and alkaline-earth elements and higher silica levels, may justify the encapsulating effect on the chromium in FBI ashes, since the amount leached by TCLP is proportionally less than expected from the higher chromium content compared to FGI ashes.

Chromium extraction from ashes by a hydrometallurgical route

Table II demonstrates high stability of chromium combination in the ashes, since chromium recoveries are very low.

Fig. 2 analyzes the results of the first set of experiments and establishes factors which influence chromium recovery by plotting a dependent variable that maximizes the signal-to-noise ratio of response, i.e. $ETA = -10 \times \log_{10}[(1/N) \times Sum(1/y^2)]$, where N is the number of experiments and y refers to the percentage of chromium recovered. The criteria for analysis is "larger-the-better", i.e., as great as possible chromium recovery, and composed output variable is that referred in YY' axis. The obvious conclusion is that more concentrated H_2SO_4 solutions, finer ashes and higher leaching temperature favour chromium recovery. This same effect for H_2SO_4 is repeated in the other set of experiments.

Perchloric acid seems not to favour significant dissolution of chromium under the tested conditions. The standard potential for oxidizing Cr(III) to Cr(VI) in acid solutions, transforming Cr_2O_3 into a soluble hydrogen-chromate species or dichromate anion, exceeds 1.3 V, and even perchloric acid seems to need more drastic conditions.[6] The efficiency of this strong oxidant is confirmed only at higher temperatures and with pure acid mixtures by the results presented in Fig. 1 showing that the volume of perchloric acid must be no less than that of sulphuric acid and that 25 or 50 ml of mixture per gram of ashes dissolves practically all of the chromium.

Chromium extraction from ashes by a pyrometallurgical and hydrometallurgical route

Figs. 3, 4 and 5 report some of the results obtained with Na_2CO_3. As can be seen, 600 °C is clearly a low operating temperature for recovery of chromium from both types of ash. However, practically all of the chromium is leached from the ashes following heating with the Na_2CO_3/ash ratio = 3 mixtures at temperatures above 700 °C and holding them for 2 hours. In the case of FGI ashes, recoveries above 80 and 90% chromium are obtained in half-hour and 1 hour of holding time, respectively.

With FBI ashes, silicon co-extraction is generally high and increases with holding time at temperatures up to 800 °C. Contrarily, it decreases for holding times longer than 30 minutes at higher temperatures. At the temperature of 900 °C there is a kind of competition between

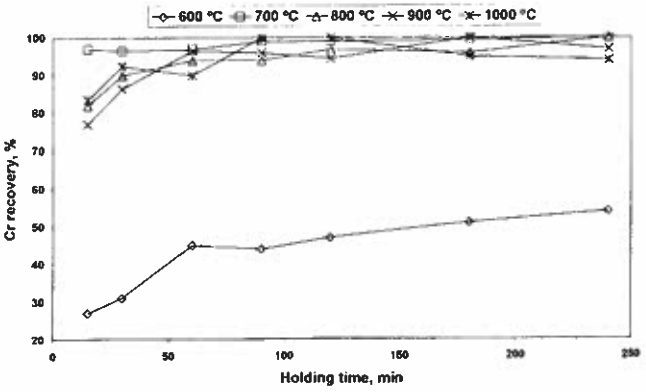

Figure 3. Chromium recovered *vs* temperature and holding time using sodium carbonate in mixtures with FBI ashes at a Na_2CO_3:ash mass ratio = 3.

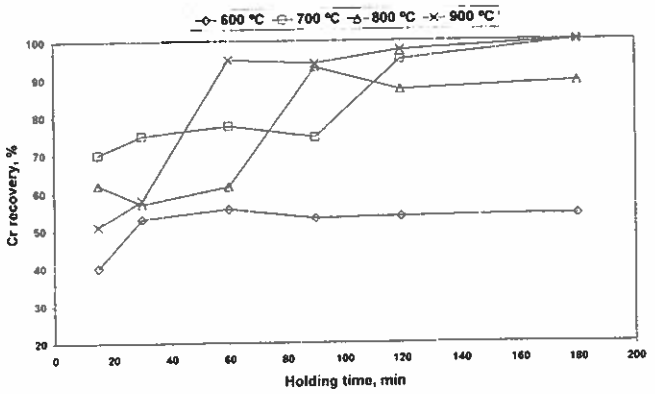

Figure 4. Chromium recovered *vs* temperature and holding time using sodium carbonate in mixtures with FGI ashes at a Na_2CO_3:ash mass ratio = 3.

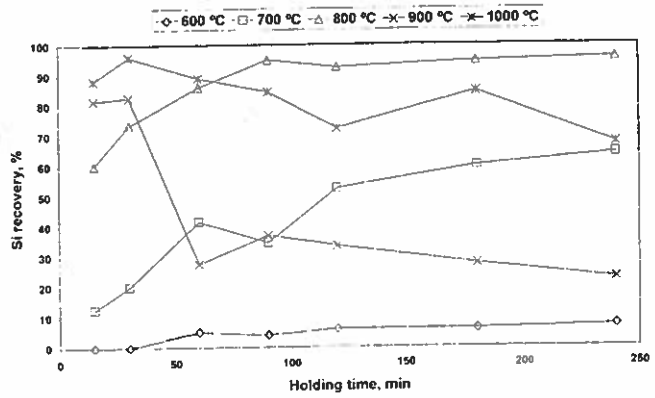

Figure 5. Silicon dissolved *vs* temperature and holding time using sodium carbonate in mixtures with FGI ashes at a Na_2CO_3:ash mass ratio = 3.

chromium and silicon, since recovery of the first increases with holding time while the recovery of the second decreases.

In general, chromium recoveries in Fig. 6 are higher than those in Fig. 4 with similar conditions of temperature and holding time. Therefore, sodium hydroxide used at reagent/ash ratio = 2 is more effective for recovering chromium from FGI ashes than sodium carbonate at a reagent/ash ratio of 3. This is an expected result since NaOH has more sodium per unit weight than Na_2CO_3 and this salt is usually very hydrated. Also, sodium hydroxide melts at lower temperature than the carbonate. However, holding times longer than

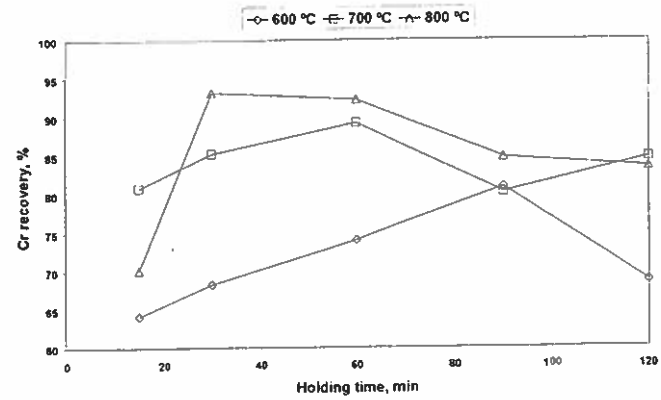

Figure 6. Chromium recovered *vs* temperature and holding time using sodium hydroxide in mixtures with FBI ashes at a NaOH:ash mass ratio = 2.

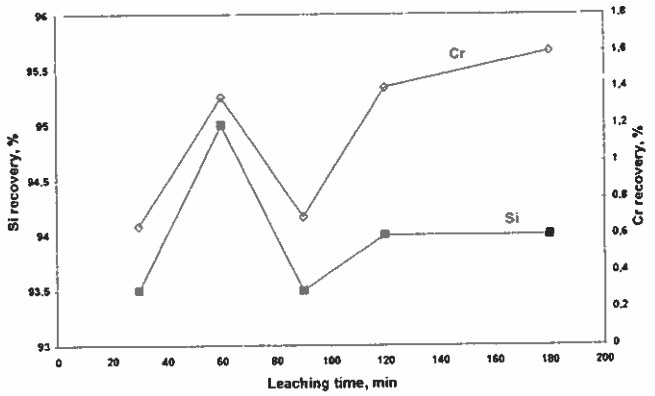

Figure 7. Silicon and chromium dissolution *vs* time for FBI ashes at the temperature of 240°C, [NaOH] = 200 g/l and ash/solution ratio = 25.

1 hour do not favour chromium recovery and a temperature of 600°C is still low to extract that metal from the ashes.

Silica leaching from the ashes

Fig. 7 summarizes the results obtained with sodium hydroxide solutions at high pressure to leach silica from FBI ashes. Leaching these silica rich ashes for 30 minutes at 240°C using a sodium hydroxide solution with 200 g/l NaOH and an ash/solution ratio of 25, dissolves practically all of the silicon and less than 2% of chromium. Consequently, this is a very effective method to upgrade leather incineration ashes.

Conclusions

Incineration of chromium sulphate tanned leather scrap in FGI and FBI pilot-combustion systems gives ashes which largely exceed the threshold value for chromium—despite the fact that it represents less than 0.2% of total chromium in the ashes. Thus, according to TCLP criteria, these ashes must be considered as hazardous wastes.

The ashes are very rich in chromium, higher than that of metallurgical and chemical grade ores, in the case of FGI ashes. Thus, ashes must be used as a useful chromium raw material. Furthermore, chromium is generally imported by countries where leather scrap is produced.

Practically all of the chromium in the FGI ashes is in a very stable form, since very strong aqueous solutions of sulphuric acid are not able to dissolve more than 2% of it. Due to the high standard potential required by Cr(III) to Cr(VI) oxidation, only mixtures of sulphuric and perchloric acids were found effective as a direct route to dissolve chromium from the ashes. However, in these mixtures the volume of perchloric acid shall be no less than that of the sulphuric acid and the solution/ashes mass ratio needs to be 5 to 10.

These highly corrosive mixtures pose problems not found at the more classic hot water alkaline route, since they require less common materials in the construction of equipment as well as additional care in the working environment and health protection.

Using the alkaline route, practically all the chromium may be leached with hot water after heating (Na_2CO_3/ash ratio = 3) mixtures at temperatures above 700°C and holding them for 2 hours. In these circum-

stances silicon co-extraction is generally high and increases with holding time at temperatures up to 800°C. Contrarily, it decreases at higher temperatures when mixtures are held longer than 30 minutes at those temperatures, a behaviour that may reflect the competition of silicon and chromium for sodium from sodium carbonate, since both metals are dissolved as alkaline salts.

Therefore, for recovering chromium, poorer silica ashes are preferable to the richer ones as well as using furnaces where a sand bed is not used. Consequently, from the point of view of chromium extraction, some care must be taken in avoiding leather scrap containing silica rich combustible residues usually produced by the leather industry, for example paper residues. Furthermore, the presence of silica is disadvantageous not only in the perspective of alkaline reagent consumption and energy spent to heat heavier mixtures, but also for the hot water leaching step, increasing silicon build up in leachate and mass of ultimate residues.

However, silicon can be selectively removed by leaching the silica containing ashes for 30 minutes at 240°C using a sodium hydroxide solution with 200 g/l of NaOH and an ash/solution ratio of 25. In these conditions practically all of the silicon is removed from the ashes with less than 2% chromium dissolution. Thus, this method is highly effective either to prepare ashes for chromium recovery or upgrade them for other uses.

Sodium hydroxide at a reagent/ash ratio = 2 seems to be more effective for recovering chromium from FGI ashes than sodium carbonate at a reagent/ash ratio of 3. This may be justified as due to the higher sodium per unit weight of NaOH and its lower melting temperature compared to the carbonate. Despite that temperatures higher than 600°C are required as well as holding times less than 1 hour to increase extraction of chromium from the ashes.

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