

Synthesis of chromium containing pigments from chromium galvanic sludges

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Abstract

In this work the screening results of the scientific activity conducted on laboratory scale to valorise chromium(III) contained in the galvanic sludge as chromium precursor for ceramic pigments are reported. The valorisation of this waste as a secondary raw material (SRM) is obtained by achievement of thermal and chemical stable crystal structures able to color ceramic material. Two different pigments pink $\text{CaCr}_{0.04}\text{Sn}_{0.97}\text{SiO}_5$ and green $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ were synthesized by solid-state reactions using dried Cr sludge as chromium oxide precursor. The obtained pigments were characterized by X-ray diffraction and SEM analysis. Furthermore the color developed in a suitable ceramic glaze was investigated in comparison with the color developed by the pigments prepared from pure Cr_2O_3 . The characterization carried out corroborates the thermal and chemical stability of the synthesized pigments and, especially for the Cr–Sn pink pigment, the powders develop an intense color that is very similar to the color developed by the pigments obtained starting from pure Cr_2O_3 .

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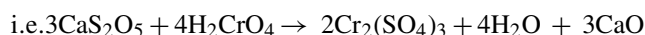
Keywords: Pigments; Chromium oxide; Galvanic sludge; Recycling

1. Introduction

The laboratory scale simulation reported in this paper aims to investigate the substitution of chromium oxide with a Cr-rich galvanic sludge in ceramic pigments production. Considering the present natural resources depletion, several researchers are looking for alternatives to transform industrial wastes and post-use products in secondary raw materials (SRM). Moreover metallic scraps and sludge, when not correctly managed, are promising sources of environmental damage.

Chromium exists primarily in trivalent [Cr(III)] and hexavalent [Cr(VI)] states in nature. These two redox states are characterized by significantly different chemical behaviour, bioavailability and toxicity [1–7]. The high toxicity (acute and chronic) and carcinogenic of chromium(VI) make this element one of the most alarming and urgent metal that needs to be controlled.

The galvanic sludge used in this work was obtained from a chromium electroplating process containing Cr as the main heavy metal. Galvanic processes, which increase corrosion-resistance properties and improve wear qualities, are based on metal plating baths and rinses. They generate effluents with a metal concentration varying with the employed process. Traditional systems reduce the toxicity of wastewater by aggregating disposed aqueous solutions of various concentrations, followed by treatment with chemicals to coagulate, flocculate and settle out solid wastes for off-site disposal [8]. In the Italian factory that kindly furnished the sludge the galvanic solution is treated with a two-stage process. The first stage reduces hexavalent chromium to the chemically unstable $\text{Cr}_2(\text{SO}_4)_3$ by using chemical reducing agents such as sulfur dioxide (SO_2), sodium bisulfate (NaHSO_3) or sodium/calcium meta-bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$).



pH is between 2 and 3.

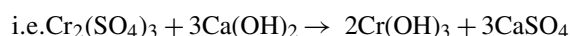
In the trivalent state chromium freely bonds to hydroxide and the final result is a non-toxic precipitate, chromium hydroxide

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Table 1
Chemical composition of dried sludge and industrial frit used

Oxide	Dried sludge (wt%)	Frit (wt%)	Oxide	Dried sludge (wt%)	Frit (wt%)
SiO ₂	0.81	61.95	TiO ₂	0.01	0.46
Al ₂ O ₃	0.80	11.80	NiO	0.05	–
CaO	15.47	12.40	CuO	0.42	–
MgO	5.64	10.40	MnO	0.01	–
Na ₂ O	1.50	0.93	CdO	0.02	–
K ₂ O	3.63	1.03	CoO	0.02	–
Cr ₂ O ₃	43.48	–	SnO ₂	–	0.7
Fe ₂ O ₃	1.18	0.30	I.L	29.18	–

Cr(OH)₃, which can be easily separated and disposed in landfills.



pH 8 or higher to obtain the hydroxides precipitation.

There are several treatments proposed in literature to avoid dumping and to recycle the galvanic wastes. Recent increase in the cost of landfill disposal and decrease in number of disposal sites have led to considerate alternatives routes and treatments. These methods can be divided into three processes: hydrometallurgical, pyrometallurgical and a mixed of both. Examples of hydrometallurgical processes are reported by Vegliò et al. [9], Odle et al. [8], Rajcevic [10] and Silva et al. [11]. Their works are related with acid leaching and metal separations with precipitation, solvent extraction or electrowinning. In the pyrometallurgical process, the majority of researches just treat wastes with restricted chemical composition of selected elements or maximum and minimum concentrations [12,13].

Another use of high temperature reactions are solidification/stabilization of chromium rich sludge, not focused on metals recovery, in cement, polymers and ceramic-based materials [14–19]. In this case, the firing step is determinant to obtain a high immobilization degree of waste. In particular the recycling

of galvanic sludge as secondary raw material for the ceramic industry could help to reduce the amount of chromium containing waste. In fact, the ceramic process presents interesting potential for wastes encapsulation purposes even in considerable amounts [20].

In this work two different ceramic pigments (pink CaCr_{0.04}Sn_{0.97}SiO₅ and green Ca₃Cr₂(SiO₄)₃) were synthesized by solid-state reactions using dried Cr sludge as chromium oxide precursor. Despite Costa et al. [21] and Berry et al. [22] report the production of ceramic pigments using chromium containing waste from leather industry, only few works have been found in literature describing the recovery of galvanic sludge as SRM.

The obtained pigments were characterized mainly by X-ray diffraction and SEM analysis, and the color developed in a suitable ceramic glaze was investigated in comparison with the color developed by the pigments prepared from pure Cr₂O₃.

2. Experimental

2.1. Sample preparation

The electroplating sludge employed in this investigation was collected from a local plant and dried at 120 °C for 24 h (water content of the sludge 68 wt%). This waste, previously milled for 40 min in a porcelain jar, was characterized by ICP spectroscopy (Varian, Liberty 200 Australia) in order to estimate the chromium content.

The synthesis of pink CaCr_{0.04}Sn_{0.97}SiO₅ and green Ca₃Cr₂(SiO₄)₃ pigments were performed using both chromium sludge and industrial Cr₂O₃ (Cr oxide content ≥ 98 wt%) as chromium precursors. The samples obtained with pure chromium oxide were used as a reference in order to establish a comparison of the color strength with a traditional pigment composition. The raw materials employed for the manufacturing of the pigments were: SiO₂, CaCO₃, a Cr oxide precursor and both Na₂B₄O₇ (5%) and NaCl (1%) as mineralizers for green; SiO₂, CaCO₃, SnO₂, a Cr oxide precursor and LiBO₂ (2%) as mineralizer for pink. These raw materials, used as received without any purification to reproduce the industrial pigment production, were appropriately weighted considering the colored phase stoichiometry and the different chromium content of the selected Cr precursors. After a dry milling step of 30 min, the so obtained mixtures were calcined for 3 h in closed porcelain crucibles at 1100 °C for the green powders and at 1000 °C for the pink mate-

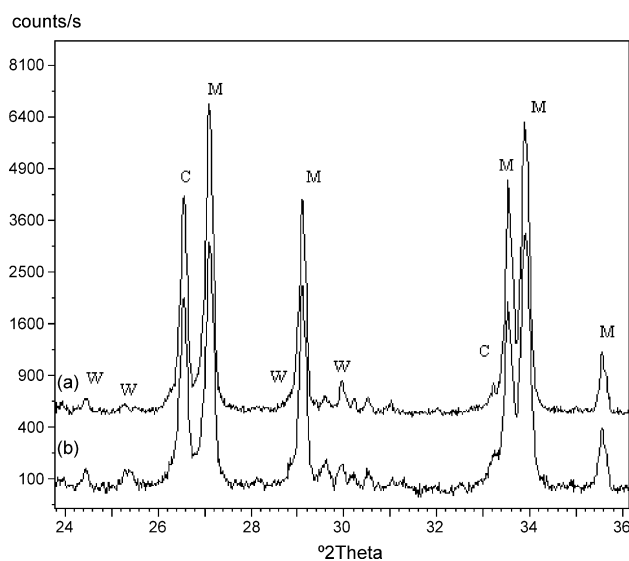


Fig. 1. XRD patterns of the pink pigments obtained starting from both galvanic waste (a) and pure Cr₂O₃ (b). C = cassiterite (SnO₂), M = malayaite (CaSnSiO₅) and W = wollastonite (CaSiO₃).

rial respectively. Then the products were wet milled for 20 min in a porcelain jar. After drying, the powders were characterized and tested as pigments for glaze coloring. A ceramic glaze, having a typical composition for high temperature (Table 1), was used for pigment application. The pigments, added to the composition at 4 wt%, were wet mixed with the ceramic frit (water content 40 wt%) for 30 min in a blender-mixer. The slips were deposited on ceramic tiles obtaining a uniform glaze layer and then fired at 1140 °C for 35 min following an industrial cycle.

2.2. Pigment characterization

In order to qualitatively examine the crystalline phases present on the calcined powdered samples, X-ray diffraction measurements (XRD) were carried out using a conventional Bragg–Brentano diffractometer (PW 3710, Philips Research Laboratories) with Ni-filtered Cu K α radiation. The patterns were recorded on the grounded samples (<25 μ m in size) in the 20–80° 2θ range at room temperature, with a scanning rate of 0.005°/s and a step size of 0.02°. The morphology and microstructure of the samples were examined by scanning electron microscopy (SEM) (XL40, Philips Research Laboratories) equipped with an energy dispersion spectroscopy (EDS) equipment (EDAX, Philips Research Laboratories).

Differential thermal analysis (TG-DTA, mod. 409, Netzsch) were performed on powders in air to evaluate the thermal stability of pigments. About 30 mg of powdered sample <25 μ in grain size has been subjected to a thermal treatment from 20 to 1400 °C at a heating rate of 10 °C/min.

Stabilization efficiency was assessed by water-leaching test (DIN 38414, liquid/solid ratio 10:1, leaching time 24 h), TCLP test (EPA method no. 1311 aqueous solution of acetic acid, pH 2.88 ± 0.05 , liquid/solid ratio 20:1, leaching time 18 h). Moreover leaching experiments with sulphuric acid 1N (liquid/solid ratio 10:1) were carried out at room temperature for 24 h in order to evaluate a very strong acid condition. A magnetic stirrer was used to ensure the full suspension of particles and improve liquid-to-solid phase contact. The heavy metals content of the solutions was determined by ICP spectroscopy.

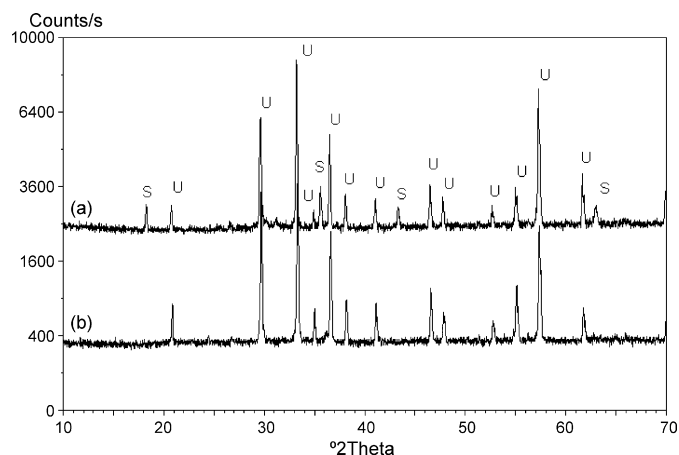


Fig. 2. XRD patterns of the green pigments obtained starting from both galvanic waste (a) and pure Cr₂O₃ (b). U = Ca₃Cr₂(SiO₄)₃ and S = (Mg, Fe)Cr₂O₄.

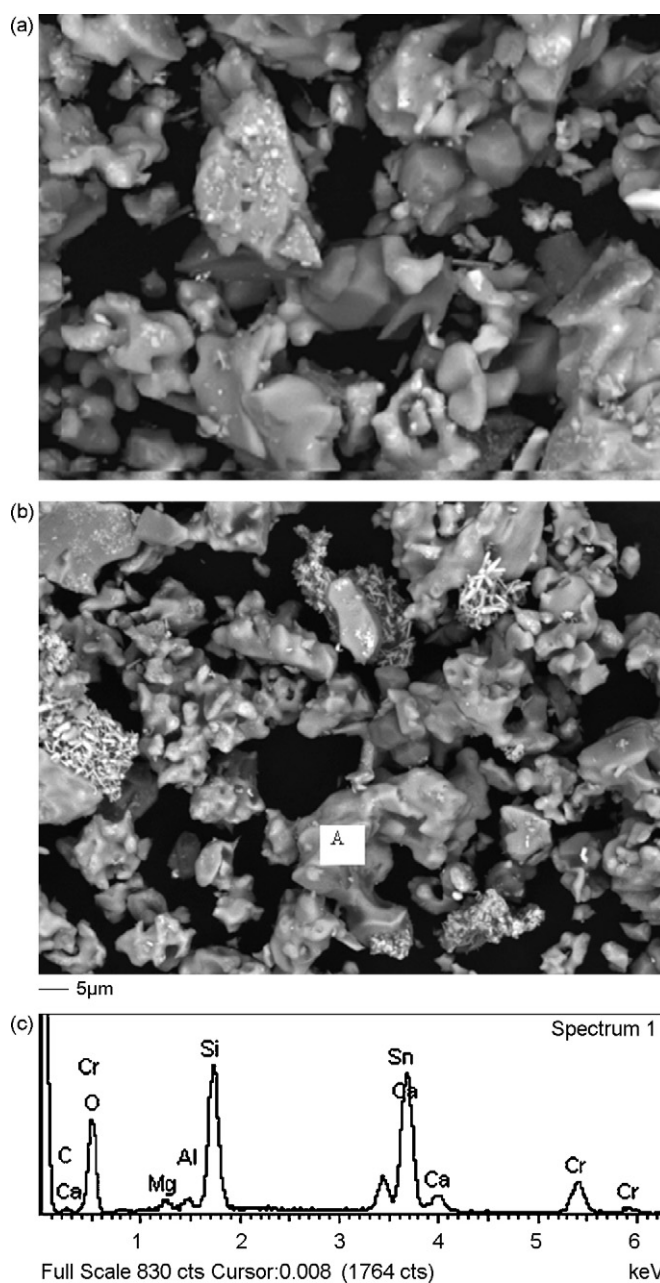


Fig. 3. SEM images of the pink pigments obtained starting from both pure Cr₂O₃ (a) and galvanic waste (b) and EDS spectra (c) of the area labelled A.

Finally, color measurements were performed on both pigments and glazes by UV–vis spectroscopy (model Lambda 19, PerkinElmer) using the CIELab method in order to obtain L^* , a^* and b^* values [23]. The method defines a color through three parameters, L^* , a^* and b^* , measuring brightness, red/green and yellow/blue color intensities, respectively [24]. The method allows, moreover, to define a color difference as ΔE^* , based on the relationship:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where ΔL^* , Δa^* and Δb^* measure the differences in luminosity and in chromaticity between two color.

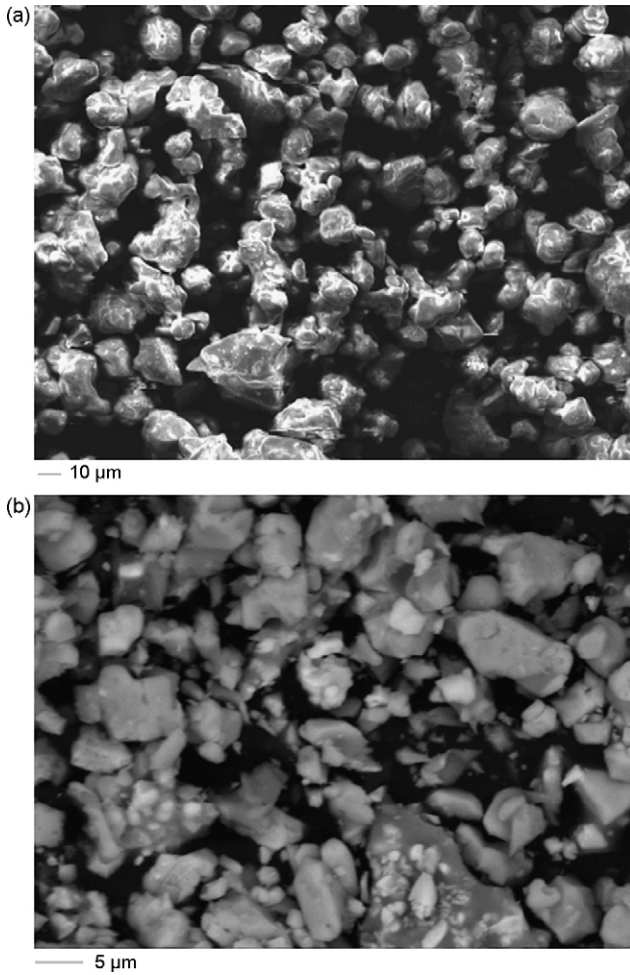


Fig. 4. SEM images of the green pigments obtained starting from both pure Cr₂O₃ (a) and galvanic waste (b).

3. Result and discussion

3.1. Galvanic sludge characterisation

The chemical analysis of the dried galvanic waste, that is amorphous from a mineralogical point of view, is reported in Table 1. The results confirm that the as received sludge contains a high percentage of Cr₂O₃ and CaO due to the precipitant agent used and suggest the potentiality of such galvanic sludge as a low-cost raw material for the preparation of the selected ceramic

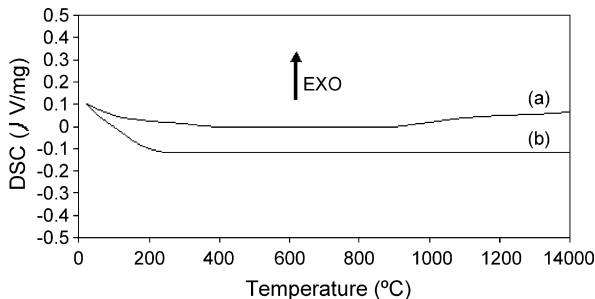


Fig. 5. DTA curves of pink (a) and green (b) pigments obtained from galvanic waste.

Table 2
CIELab values of the obtained pigments

Pigment	L*	a*	b*
Pink from sludge	49.67	11.69	2.52
Pink from Cr ₂ O ₃	50.07	11.85	1.84
Green from sludge	46.64	-1.40	3.36
Green from Cr ₂ O ₃	43.67	-3.92	5.00

pigments. The high weight loss on ignition (around 30 wt% at 1200 °C) is due to the decomposition of crystallised phases with CO₂ and H₂O formation as determined by the authors [25].

3.2. Pigments characterisation

Fig. 1 reported the XRD patterns of the obtained pink powders. The mineralogical comparison indicates no variation of the main crystalline phases when galvanic powders or pure Cr₂O₃ are employed. In fact Fig. 1 shows the presence of malayaite CaSnSiO₅ (ICDD 25-0176), wollastonite CaSiO₃ (ICDD 27-0088) and nonreacted cassiterite SnO₂ (ICDD 27-0088) as main crystalline phases in both pigments.

The XRD patterns of the green pigments put in evidence slight differences between the powder obtained starting from the chromium sludge (Fig. 2a) and that obtained starting from pure chromium oxide (Fig. 2b). In fact, beside uvarovite (Ca₃Cr₂(SiO₄)₃, ICDD 01-087-1007), which is the main colored structure in pattern a, a spinel phase (Mg, Fe)Cr₂O₄ (ICDD 01-071-1256) not present in the pattern of powder obtained starting from pure chromium oxide, was also identified.

SEM observations, reported in Fig. 3a and b, indicate that the microstructure of the pink pigment powders does not vary using

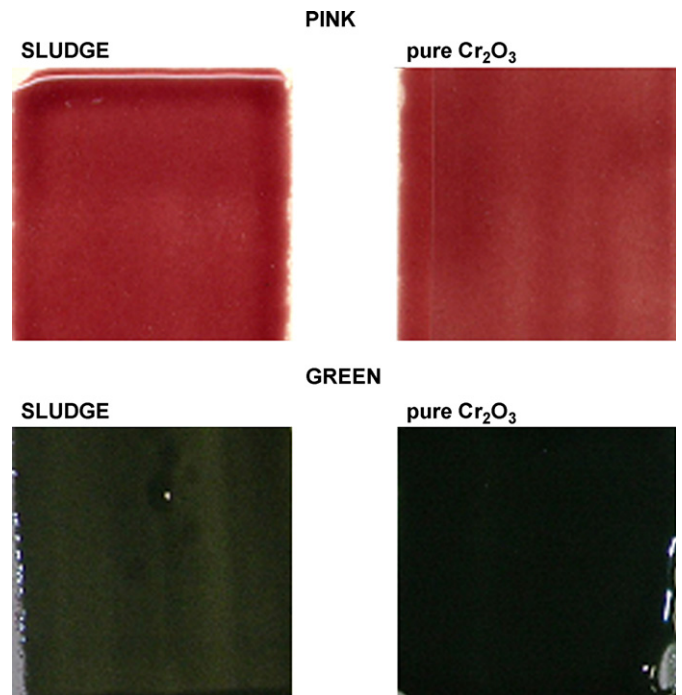


Fig. 6. Colored glazed tiles obtained with the synthesized pigments.

Table 3
CIELab values of the obtained glazes

Glaze	L^*	a^*	b^*
Pink from sludge	48.06	24.34	8.52
Pink from Cr_2O_3	47.73	23.52	8.20
Green from sludge	40.24	-2.85	8.34
Green from Cr_2O_3	35.04	-7.40	11.87

either Cr_2O_3 or galvanic waste as chromium precursors. In fact, independently on the chromium precursor used, the images show the formation of Ca–Sn–Si rich crystals, as evidenced by EDS analysis (Fig. 3c) with an homogenous and narrow grain size distribution centred at around $10\ \mu\text{m}$. In particular, Fig. 3c also shows the presence, of needle-shaped crystals of wollastonite, which is in accordance with XRD patterns.

Fig. 4 shows the microstructures of the green pigments. The pigment obtained starting from pure chromium oxide (Fig. 4a) shows a homogeneous microstructure constituted by particles with a narrow grain size distribution centred at around $10\ \mu\text{m}$. The pigment obtained by sludge, instead, presents a wide grain size distribution (Fig. 4b) with hard agglomerates. The curves of differential thermal analysis reported in Fig. 5 indicate that the pigments show a high stability up to $1400\ ^\circ\text{C}$ since no peaks appear in the temperature range investigated.

The successful formation of the coloring phases was also confirmed by colorimetric analysis (Table 2). For the synthesized pigment, the a^* parameter, in relation to the scale extending from green ($-a^*$) to red ($+a^*$), is undoubtedly the most significant parameter for defining the powders color. Table 2 shows that the pink powders had a high $+a^*$ value independently to the chromium oxide precursor used. The other color parameters, L^* and b^* , are also quite similar. The green powders, instead, have $-a^*$ values very different with the pigments obtained starting from pure eskolaite that developed a more intense hue. The color developed by these pigments added at 4 wt% in an industrial glaze for high temperature (Fig. 6) is reported in Table 3. Regarding the pink pigment, the table shows that the obtained powders develop a good red shade in the glaze, irrespective of the raw materials used (hue variation, $\Delta E^* = 1.98$), indicating the chemical and thermal stability of the synthesized powders. Instead, the L^* , a^* and b^* parameters of the green glazes demonstrate a significant difference in color. In this case, the glaze hue variation is very high ($\Delta E^* = 7.75$) and it can be attributed to the crystalline phases developed as evidenced in the XRD patterns.

All leaching tests performed on powdered glazes indicate removal levels of toxic elements clearly under the legal safety limits (amounts lower than $0.05\ \text{ppm}$).

4. Conclusion

This work confirms the possibility to use galvanic sludge as chromium oxide precursor for the development of Cr-based ceramic pigments. The characterization carried out corroborates the thermal and chemical stability of the synthesized powders and, especially for the Cr–Sn pink pigment, the powders develop an intense color that is very similar to the color developed by

the pigments obtained starting from pure Cr_2O_3 . Concerning the green pigments, the L^* , a^* and b^* parameters of the glazes are significantly dissimilar due to the differences emerged by XRD. For this system, thus, further work should be done to optimize the synthesis parameter such as calcination temperature and time.

Nevertheless in the synthesis of these pigments, chromium(III) was stabilized within an inorganic crystalline matrix at high temperature avoiding oxidation to toxic chromium(VI). This could be considered an important technological result both from an economical and environmental point of view considering the strict limitations and the expense of the disposal of chromium(II).

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