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on Fundamental and Applied Aspects of
Physical Chemistry

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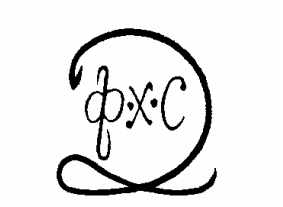

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BLACK INORGANIC PIGMENTS OBTAINED FROM WASTE MATERIALS

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ABSTRACT

Hazardous industrial wastes are the most common source of environmental pollution. Waters originating from unregulated landfills and places of inadequate disposal of this type of wastes can pollute the water sources and affect the human health. In this study, electroplating waste sludge (ES) and various Fe-rich wastes were used as starting materials for the synthesis of inorganic pigments. Obtained black $Cr_{1.3}Fe_{0.7}O_3$ pigments possess adequate properties required for use as inorganic pigments.

INTRODUCTION

Inorganic pigments are widely applied due to the many of their advantages: high chemical and temperature stability, non-toxicity, resistance to the influence of UV radiation, and as such, can be used for external uses: facades, roofs, wall and floor tiles [1,2]. The waste sludge used in this study comes from an electroplating plant (nickel, chromium, zinc, etc.) and belongs to toxic industrial wastes class. It has already been used [3] as a raw material for the synthesis of black inorganic pigment through the reaction with commercially available Fe_2O_3 (p.a. purity). Despite expectations that a spinel ($FeCr_2O_4$) black pigment will be obtained, it was found that a mixed Fe/Cr oxide ($Cr_{1.3}Fe_{0.7}O_3$) was obtained instead. However, its color and non-toxicity indicate the possibility for his commercial use. In this study, we tried to replace previously used p.a. Fe_2O_3 with a various Fe-rich wastes as cheaper raw materials, thus fully following the principles of circular economy.

EXPERIMENTAL

The ES investigated in this study was collected from an open-air basin containing 40t of historical sludge from the Cr/Ni-plating plant of "PPT TMO" Technological and metallurgical processing factory, Trstenik, Serbia. As a Fe-source, following waste materials, in the form of the powders, were used in this study: Fe-waste from the metal processing industry (FeW1); Fe-waste from the steel plant (FeW2); Rust, scraped from the iron/steel items that were exposed to atmospheric conditions for a longer period (FeW3).

Characterization of the Cr/Ni plating sludge and products obtained from it, included determination of chemical composition (XRF), main crystalline phases (XRD), color of the samples (UV/VIS, NIR) expressed in L*a*b* values and toxicity level (leaching test, performed according to DIN-38414-S4, to determine the metals mobility under the neutral conditions [4]).

RESULTS AND DISCUSSION

The sludge in liquid form was taken from a basin at five different spots and then thoroughly mixed while in liquid state. Sludge was then dried at 110 °C and the mass of the dry residue was measured. It was found that water content in sludge is about 91.5 wt%. Chemical composition of the dried sludge is shown in Table 1 and it represents average value of five different samples.

Table 1. Chemical composition of the dried ES determined by XRF

	Cr	Fe	P	Zn	Ni	Cu	Pb	Si	Elements in traces
Conc. (wt%)	62.93	11.79	9.20	6.51	3.58	2.62	1.75	1.36	0.26

From the XRD patterns (not shown) of the dried (110 °C) and calcined (600 °C) Fe-wastes, following was observed: all reflections in the XRD pattern of the dried FeW1 waste can be ascribed to Fe_2O_3 phase (JCPDS No. 33-0664). XRD patterns of dried FeW2 waste showed reflections of the Fe_2O_3 phase and Fe_3O_4 phase (JCPDS No. 19-0629). XRD patterns of dried FeW3 waste showed reflections of the species that are known as the rust constituents: FeO-OH (JCPDS No. 76-2301), $Fe(OH)_3$ (JCPDS No. 38-0032) and Fe_3O_4. After the calcination at 600 °C, XRD patterns of all Fe-wastes showed reflections originating only from the Fe_2O_3 phase, indicating that all the wastes constituents were transformed into the Fe_2O_3 during the calcination process. Moisture content i.e. weight loss after drying at the 110 °C were 0 wt% for FeW1, 0 wt% for FeW2 and 2.2 wt% for FeW3. Weight losses after the calcination at 600 °C were 0 wt% for FeW1, 0 wt% for FeW2 and 6.6 wt% for FeW3.

By varying the amount of the Fe-waste added into the ES, it was found that for all Fe-wastes, 30 wt% is amount that is sufficient to transform ES into the black pigment.

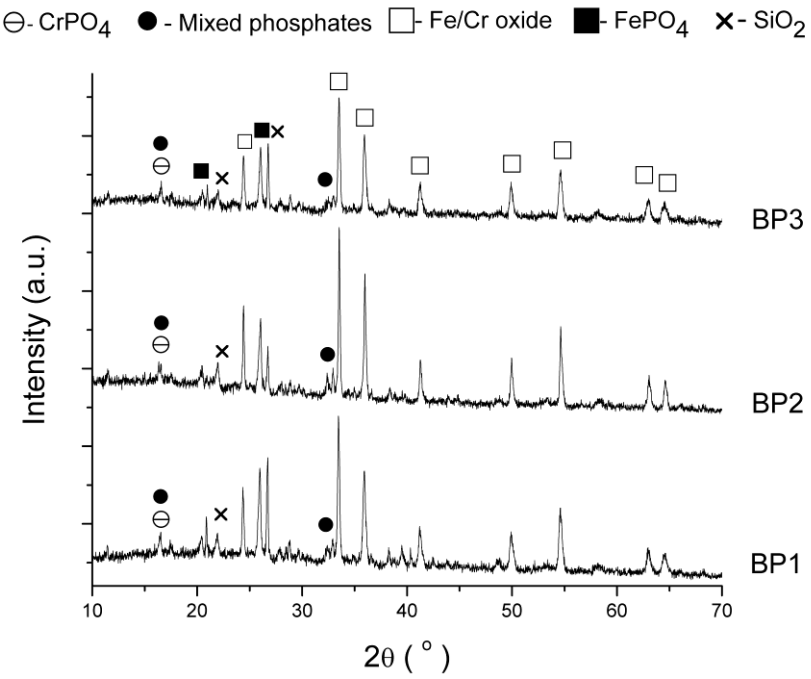

Figure 1. XRD patterns of the black pigments obtained after the calcination of various ES/Fe mixtures at 1000 °C (2h): BP1 – ES/30wt% FeW1; BP 2 – ES/30wt% FeW2; BP 3 - ES/30wt% FeW3.

As can be seen from Fig. 1, $CrPO_4$ and mixed phosphates phases, which are characteristic for unreacted ES, almost completely disappeared. Dominant phase in all pigments was $Fe_{0.7}Cr_{1.3}O_3$ mixed oxide, followed by $FePO_4$ and SiO_2 phases. Also, there were no reflections characteristic for the bulk/metallic Fe or Fe_2O_3 phase, which indicated that all Fe was bounded either in $Fe_{0.7}Cr_{1.3}O_3$

mixed oxide structure or in $FePO_4$ structure. Color of all the samples was black without brown domains in it.

Color of the pigments was estimated by UV/VIS spectroscopy and Table 2 shows the colorimetric coordinates of some pigments. As one can see, values for L*a*b* coordinates are in accordance with the literature, or even better. (L = 100 = white color; L = 0 = black color).

Table 2. The colorimetric coordinates of black pigments

	L*	**a***	**b***
BP1	38.00	0.44	-1.99
BP2	38.29	0.22	-2.24
BP3	38.35	0.48	-2.04
Commercial black pigment [1]	33,0	1	0
Commercial black pigment [3]	28,8	-1,2	0,7

Level of toxicity, i. e. the leaching test, was conducted according to DIN-38414-S4 standard, which is most commonly found in the literature regarding the synthesis of pigments from waste materials. The metal concentrations in eluates were determined by the AAS method (Atomic Absorption Spectroscopy) and the results are shown in Table 3.

Table 3. Metal content (mg/l) in eluates obtained after the leaching test

	Cr	**Ni**	**Pb**	**Zn**	**Fe**	**Cu**	**pH**
ES dried at 110 °C	10,5	75	0,1	194	69	9,1	4,5
BP1	<0,01	<0,2	<0,5	<0,1	0,32	<0,1	7,7
BP2	<0,01	<0,2	<0,5	0,11	<0,3	<0,1	7,1
BP3	<0,01	<0,2	<0,5	<0,1	<0,3	<0,1	6,9
Allowed concentrations*	***0,05 - 1***	***0,04 - 1***	***0,05 - 1***	***0,4 - 5***	***/***	***0,2 - 5***	***4 – 13***

***** - EU Council Decision 2003/33/EC; first value refers to the ***"Inert"*** and second to the ***"Non-hazardous"*** classification of materials

CONCLUSIONS

Following the principles of the circular economy, black $Fe_{0.7}Cr_{1.3}O_3$ pigments were obtained using only the waste materials (electroplating sludge and Fe-rich wastes). The obtained products show no leaching of toxic metals, have color comparable to those of commercial pigments and thus have potential commercial application.

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