# DEVELOPMENT OF CERAMIC PIGMENTS FROM WASTE STREAMS RICH IN ZINC AND COPPER

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## 1. INTRODUCTION

In this study, pigments were developed with zinc and copper oxides obtained from waste products of industrial processes in different sectors located in the Valencia Region, such as the children's and leisure products (toys) sector and the metal-processing sector. Applying innovative technologies to various environmental aspects (waste and wastewater) of these sectors, secondary raw materials (zinc and copper oxides) were obtained that have been used in developing ceramic pigments.

The children's and leisure products (toys) and metal-processing sector generate high volumes of waste streams rich in copper and/or zinc, which are currently managed as waste:

- The copper-rich streams (>500 ppm) come from baths for treating textiles and metal and plastic surfaces (stripping processes), used to modify surface characteristics and to provide surfaces with new properties.
- The zinc-containing products come from the zamak-obtainment process and from electrolytic baths (acid stripping processes).

Treating these streams enables the material (Cu or Zn) to be recovered from the waste, which directly benefits the environment, reducing landfill disposal (which often exhibits high acidity or basicity and the presence of numerous heavy metals), as well as the primary obtainment of these metals and their derivatives.

## 2. MATERIALS AND METHODS

The waste used came from treatment of spent streams of a metal-processing sector company that makes electrolytic coatings. After treatment of these streams (chemical treatment, filtration, electrodeposition, calcination, etc.), two secondary raw materials (waste Zn and waste Cu) were obtained, which were used to produce ceramic pigments.

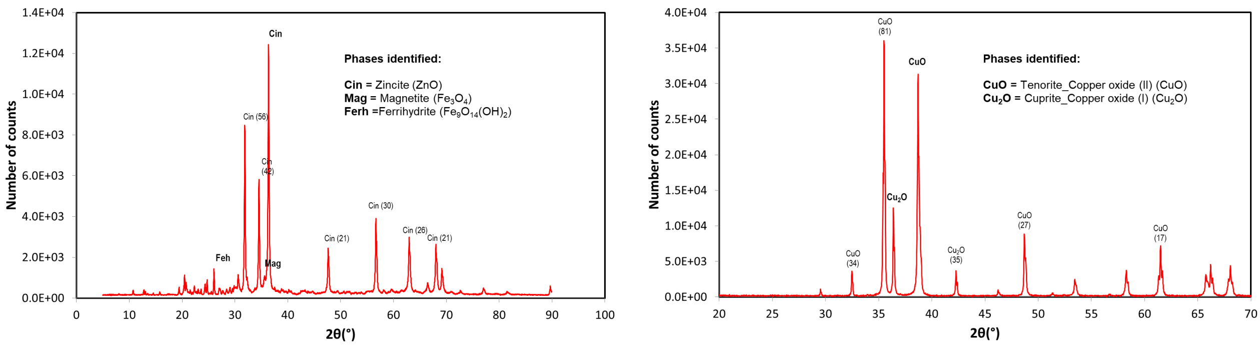
The metals were analysed, using X-ray fluorescence (XRF) to verify their degree of purity and the different metals they might contain. After calcination, X-ray diffraction (XRD) was carried out on the oxides obtained. The results were used to develop ceramic pigments with the secondary raw materials obtained, and the resulting pigments were compared with pigments of the same composition obtained from pure oxides. Finally, the pigments obtained were used in preparing coloured glazes and the colouring strength of each pigment was compared with that of the pigment synthesised with pure oxides.

## 3. RESULTS

The analysis of the wastes obtained prior to calcination is detailed in Table 1. Figure 1 shows the crystalline phases of the two wastes, obtained after their calcination.

| | Zn waste | Cu waste |
|---|---|---|
| **Cu** | 2.2 | 100 |
| **Zn** | 96.8 | - |
| **Fe** | 0.9 | - |

***Table 1.*** *Analysis of the secondary raw materials (waste) obtained prior to calcination by X-ray fluorescence.*




*a) Zn waste* *b) Cu waste*

***Figure 1.*** *Crystalline phases of the two wastes after calcination.*

The wastes characterised were used to obtain two pigments, each of which was introduced into a respective glaze. The results were compared with analogous pigments, obtained from pure oxides.

## ZN-FE-CR BROWN PIGMENT

Pigments ME and MER were formulated, equalling the chemical composition, and they were obtained according to the same procedure and calcination cycle. Figure 2 shows the diffractograms of the calcined pigments, as well as their appearance. The pigment obtained with pure oxides (ME) exhibited the highest spinel peak, in addition to displaying a zinc oxide peak in its analysis.

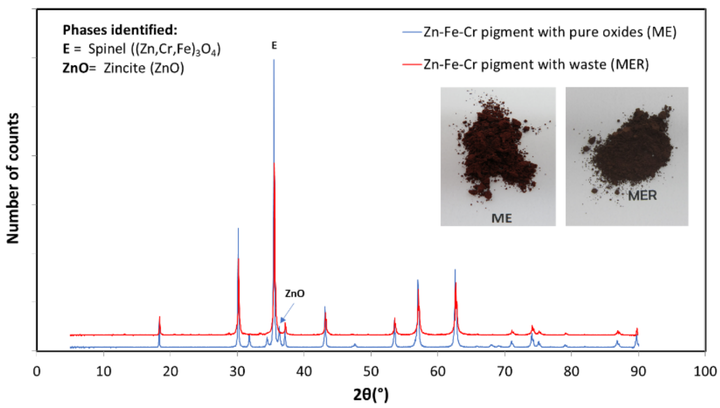
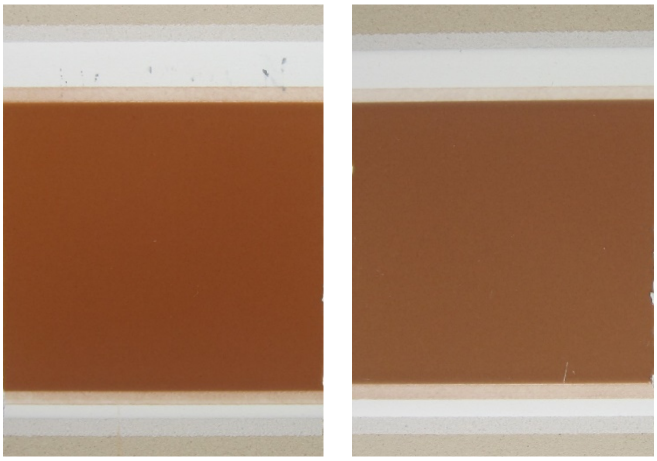



***Figure 2.*** *X-ray diffraction of Zn-Fe-Cr pigments obtained with pure oxides (ME) and with Zn waste (MER).*

The two pigments were then used to prepare porcelain stoneware tile glazes with a matt finish. Table 2 details the results of the chromatic coordinates and gloss of the two glazes. In addition, Figure 3 shows the appearance of these glazes at a firing temperature of 1200ºC.

| Glaze | L* | a* | b* | Gloss 60° |
|---|---|---|---|---|
| **ME** | 52.6 | 16.9 | 20.8 | 28 |
| **MER** | 51.1 | 14.3 | 15.7 | 30 |

***Table 2.*** *Chromatic coordinates and gloss of the glazes obtained with the different pigments (1200°C).*



*a) ME* *b) MER*

***Figure 3.*** *Appearance of the glazes obtained with the two pigments (Glaze firing temperature: 1200°C).*

## CU-CR BLACK PIGMENT

Pigments NE and NER were formulated, equalling the chemical composition, and they were obtained according to the same procedure and calcination cycle. Figure 3 shows the diffractograms of the calcined pigments, as well as their appearance. First, the background of the diffractogram is observed to be higher than in the pigments of the previous section (Zn-Fe-Cr brown) because the black pigment composition contained copper. The same crystalline phases appeared in both pigments. However, the diffraction peak at 2Theta=31.37º corresponding to the Mcconnellite was stronger in the NER pigment, probably because it had a different crystallinity or had crystallized in some preferred orientation. In addition, the NER pigment exhibited tenorite (CuO), which was not detected in the pigment formulated with pure oxides (NE).

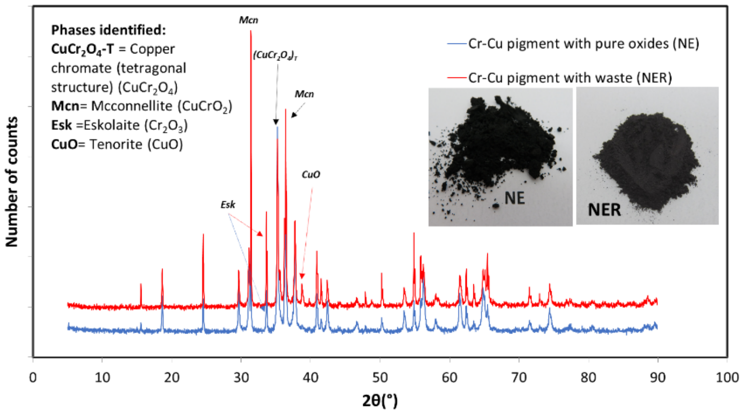
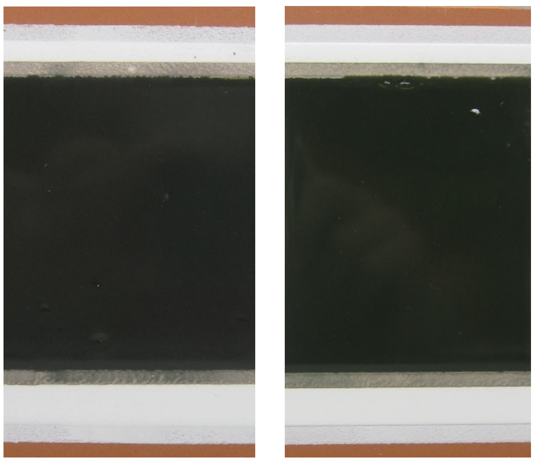



***Figure 4.*** *X-ray diffraction results of the Cu-Cr pigments obtained with pure oxides (NE) and with the Cu product (NER).*

The two pigments were then used to prepare glazes that gave rise to a glossy finish. Table 3 details the results of the chromatic coordinates and gloss of the two glazes. Figure 5 shows the appearance of these glazes at a firing temperature of 980ºC.

| Glaze | L* | a* | b* | Gloss 60° |
|---|---|---|---|---|
| **NE** | 30.9 | -1.1 | 1.3 | 76 |
| **NER** | 30.8 | -2.7 | 3.0 | 82 |

***Table 3.*** *Chromatic coordinates and gloss of the glazes obtained with the different pigments (980°C).*



*a) NE* *b) NER*

***Figure 5.*** *Appearance of the glazes obtained with the two pigments (Glaze firing temperature: 980°C).*

## 4. CONCLUSIONS

The glazes obtained with the pigments prepared with pure oxides (ME and NE) exhibited slightly different shades from the analogous glazes obtained with the products made from waste. However, the surface appearance of the glazes obtained using waste displayed no contaminations or defects. These results indicate that, although the pigment obtainment conditions for equalling the fired glaze colour need to be adjusted, the wastes from waste streams of other industrial sectors are a valuable alternative to the use of pure oxides in ceramic pigment manufacture.

The results obtained have evidenced the feasibility of using the waste products studied in manufacturing sustainable pigments that can be used in producing tiles, thus reducing the use of conventional raw materials and contributing to reducing the environmental impact associated with these processes.

## 5. ACKNOWLEDGEMENTS

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## 6. REFERENCES

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