



# Synthesis and characterization of hematite pigment obtained from a steel waste industry

S.R. Prim<sup>a</sup>, M.V. Folgueras<sup>a,\*</sup>, M.A. de Lima<sup>a</sup>, D. Hotza<sup>b</sup>

<sup>a</sup> Department of Mechanical Engineering, University of the State of Santa Catarina, Santa Catarina, Brazil

<sup>b</sup> Departamento de Engenharia Química, Federal University of Santa Catarina, Santa Catarina, Brazil

## ARTICLE INFO

### Article history:

Received 23 March 2011

Received in revised form 13 June 2011

Accepted 14 June 2011

Available online 23 June 2011

### Keywords:

Iron-based ceramic pigments

Hematite-silica

Waste valorization

## ABSTRACT

Pigments that meet environmental and technology requirements are the focus of the research in the ceramic sector. This study focuses on the synthesis of ceramic pigment by encapsulation of hematite in crystalline and amorphous silica matrix. Iron oxide from a metal sheet rolling process was used as chromophore. A different content of hematite and silica was homogenized by conventional and high energy milling. The powders obtained after calcinations between 1050 and 1200 °C for 2 h were characterized by X-ray diffraction and SEM analysis. The pigments were applied to ceramic enamel and porcelain body. The effect of pigment was measured by comparing  $L^*a^*b^*$  values of the heated samples. Results showed that the color developed is influenced by variables such as oxide content employed, conditions of milling and processing temperature. The results showed that the use of pigment developed does not interfere in microstructural characteristics of pigmented material. The best hue was obtained from samples with 15 wt% of chromophore, heated at 1200 °C in amorphous silica matrix.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Metal industries contribute significantly to the generation of waste. Thus, these industries show growing support for studies that research the use of these materials for applications in other processes, adding value to materials that are treated as waste [1].

The production of iron oxide pigments might become one approach for reducing the problem of these industries because they generate waste with high content of iron in the form of oxides and metals in their processes.

The use of these iron-rich materials is essential due to growing demand for new pigments, driven by the increase in construction activities. The importance of iron oxide pigments is also based on their non-toxicity, chemical stability, durability, variety of colors and particularly their low cost for emerging markets and a growing concern about the use of heavy metals in pigment production [2].

This environmental awareness is regarded with great interest by the industry, leading to the development of ceramic pigments with high stability and intense hues. These pigments will also meet technological and environmental requirements. In turn, this might lead to the development of more economical and efficient processes thus allowing for the production of new pigments with intense

hues. These results might take place mainly by improving the characteristics of the pigments already used [3]. Many of the studies developed to reuse industrial wastes as ceramic pigments include the reuse of waste from the process of electroplating. Examples of these applications are reported in studies by Ferreira and Castanho [4], Milanez [5], Gomes [6], Costa et al. [7] and Casagrande et al. [8]. Additionally, studies on the incorporation of other types of waste from iron and steel have been carried out [9,10,2].

This paper aims to investigate the possibility of reuse of the waste from the rolling industry in the production of ceramic pigments.

## 2. Experimental

### 2.1. Pigment synthesis

The waste employed in this investigation was obtained from metal sheet treatment process (ArcelorMittal). This waste was used in the same condition as when collected. Crystalline (quartz) and amorphous silica was employed as raw material for the matrix.

In the formulation of pigments, the content of hematite added was of 5–15 wt%. These samples were subject to wet milling (alcohol), using conventional and high energy (300 rpm) milling for 4 h for both methods of milling. After that, the mixtures were calcined for 2 h in porcelain crucibles at 1050–1300 °C. Then the products were sifted through a 325 mesh screen.

The powders obtained were characterized and tested as ceramic pigments. A ceramic enamel and a porcelain body, composition

\* Corresponding author. Tel.: +55 474 009 7834; fax: +55 474 009 7940.

E-mail addresses: [dem2mvf@joinville.udesc.br](mailto:dem2mvf@joinville.udesc.br), [lenavf@uol.com.br](mailto:lenavf@uol.com.br) (M.V. Folgueras).

**Table 1**  
Base glaze formula (Portobello, 2009).

Raw material	Descrição	Enamel (wt%)	Porcelain (wt%)
Refractors	Alumina and Zirconium silicate	5.00	–
Hues	Wollastonite and Dolomite	11.50	–
Additives	Glue and Deffloculant	0.50	–
Frits	Ca and Zn mattes	57.00	–
Suspension agents	Kaolin and Bentonite	12.00	40
Feldspats	Potássim and Sodium	14.00	60

(Table 1), was used for the application of pigment. The pigments content added to the composition of 2 wt% for ceramic enamel and 3 wt% for porcelain body. These were fired at 1188 °C for 39 min for enameled and 1214 °C for 50 min for porcelain pieces, in accordance with industrial cycles.

## 2.2. Characterization techniques

In order to evaluate the thermal stability of the residue, a differential thermal analysis (TG-DTA) was performed on the iron oxide in oxidizing atmosphere.

The morphology of the samples of the pigments was examined by scanning electron microscopy (SEM). The samples were prepared in ultrasound (mod. C/T, Thonson) using alcohol as dispersant.

In order to examine the crystalline phases present, X-ray diffraction measurements were carried out on the calcined powdered samples using a conventional diffractometer. The interpretation of the diffractogram was done using the ICDD database (International Centre for Diffraction Data).

Color measurements were performed in fired pieces by colorimeter using the soft-spectr Magic software in a Spectrophotometer (model CM 3600d, Minolta) using the CIELab method. The color is defined through the parameters  $L^*a^*b^*$ , where  $a^*$  represents the change from green (negative values) to red (positive values);  $b^*$  represents the change from blue (negative values) to yellow (positive values). The parameter  $L^*$  define the brightness. The tests were performed at the Portobello company.

## 3. Results and discussion

### 3.1. Hematite characterization

The chemical analysis is described in Table 2. The results show that hematite contains a high percentage of  $\text{Fe}_3\text{O}_2$ , indicating that

**Table 2**  
Chemical composition of Hematite.

Oxide	Wt (%)
$\text{Al}_2\text{O}_3$	0.25
CaO	0.02
$\text{Fe}_2\text{O}_3$	97.3
$\text{K}_2\text{O}$	0.05
MgO	0.08
MnO	0.25
$\text{Na}_2\text{O}$	0.03
$\text{P}_2\text{O}_5$	0.03
$\text{SiO}_2$	0.87
$\text{TiO}_2$	0.04
BaO	0.74
$\text{Co}_2\text{O}_3$	N.D.
$\text{Cr}_2\text{O}_3$	<0.1
PbO	N.D.
SrO	N.D.
ZnO	N.D.

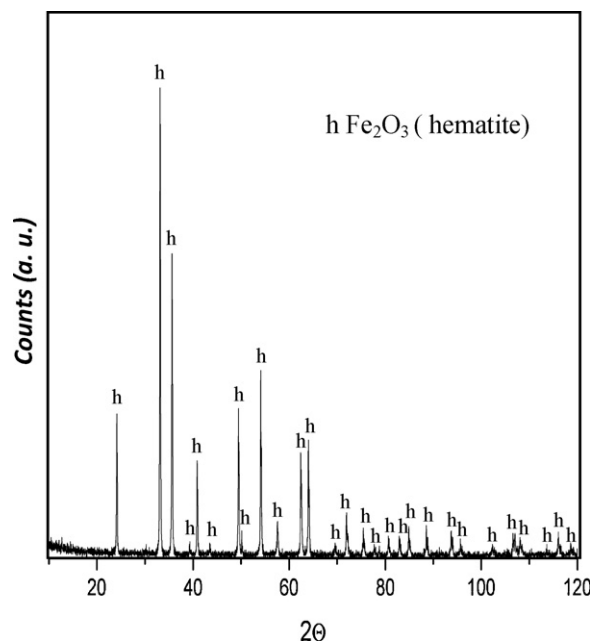


Fig. 1. XRD patterns of the hematite.

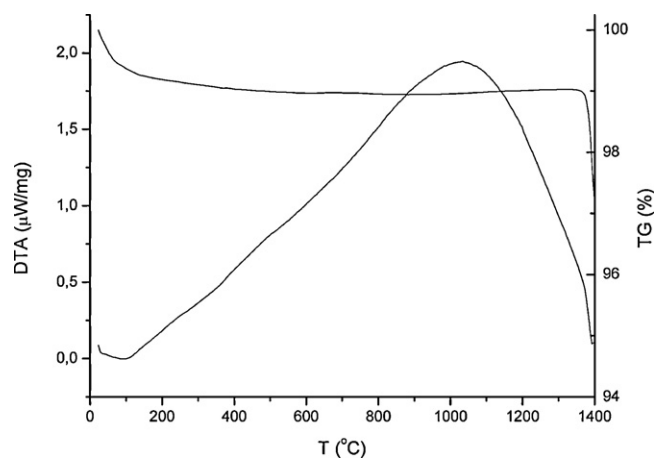


Fig. 2. DTA curve of the hematite.

this waste is an important low-cost raw material for the preparation of ceramic pigments.

Fig. 1 shows the XRD patterns of hematite present only iron oxide, in the shape of hematite (ICDD, 73-0603). Its low particle size, typical of materials from a chemical process of precipitation, favors the formation of the oxide.

The differential thermal and gravimetric analysis of hematite was performed in an oxidizing atmosphere. The purpose of performing the analysis was to identify the possible presence of phase other than hematite, as this would be subjected to oxidation process, with consequent effects associated with weight gain. The results showed that in range between 200 and 1350 °C the effect of weight gain was not identified (Fig. 2).

### 3.2. Pigments characterization

In order to evaluate the effect of the percentage of hematite in the thermal behavior of mixtures (quartz-hematite) the phases present after milling and sintering were analyzed. The limit of 15 wt% of chromophore added was defined based on literature [6,10–12]. The increase in the percentage of hematite had no influ-

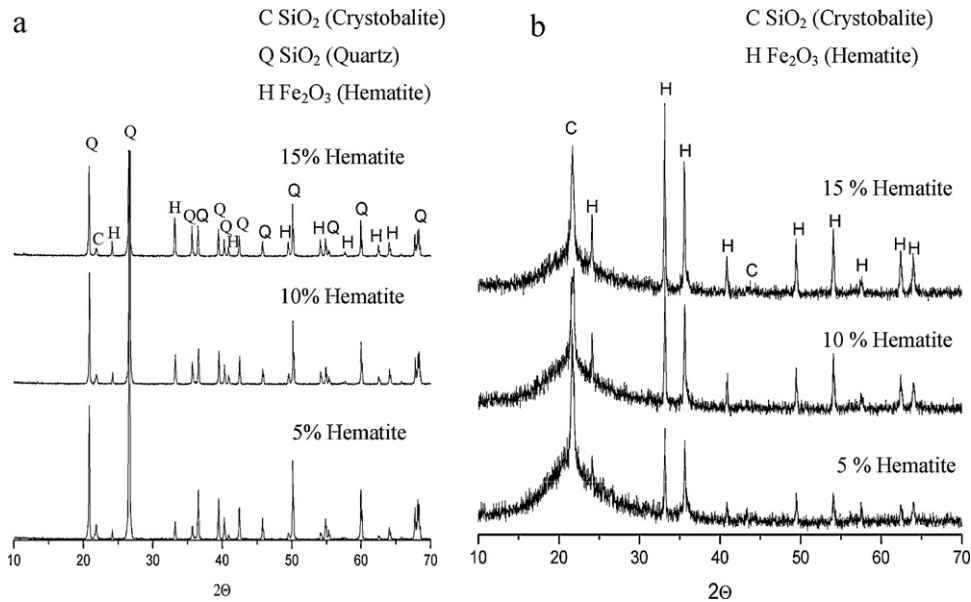


Fig. 3. XRD patterns of the samples with of 5, 10 and 15 wt% of hematite, mixed for ball milling, fired at 1200 °C. (a) Quartz matrix. (b) Amorphous matrix.

ence in the crystalline phases present after fired at a temperature range of 1050–1300 °C. The XRD patterns show this behavior for the 1200 °C temperature of sintering (Fig. 3a). The same behavior may be seen for the encapsulation process in a amorphous silica matrix, that shows the cristobalite (ICDD, 27-0605) and the hematite (ICDD, 73-0603) as main phase, as may be seen in Fig. 3b. The difference in this case is the presence of amorphous halo between 10° and 35°.

Fig. 4a and b shows the XRD patterns of the temperature effect on the phases present in the material in which 15 wt% of hematite had been added for both matrices. These matrices were subject to conventional milling and fired at a temperature range of 1050–1300 °C.

In the pigments that are encapsulated in quartz matrix, there is an increase of the relative intensity of peaks. This effect is typical of the presence of cristobalite. This is also demonstrated by a reduced

intensity of peaks corresponding to the presence of quartz (Fig. 4a). In the pigments that were encapsulated in an amorphous matrix, the presence of cristobalite is evidenced by increase of the intensity of the peaks of this phase (Fig. 4b). It can also be noted that the increase in temperature of heat treatment favored the formation of cristobalite for both systems.

SEM observations, described in Fig. 5a, indicate that when the quartz matrix was used, neither the range of temperature nor the milling process enabled the sintering effect. The particles show irregular shapes, demonstrating that the sintering effect did not take place. The same behavior was observed for other temperatures used, including for the material mixed by high energy milling. On the other hand, a higher efficiency was achieved for the amorphous silica matrix as can be seen in Fig. 5b. This matrix was subject to the same firing process and temperature as the one using for the quartz matrix. In fact, it seems that for the amorphous silica matrix tem-

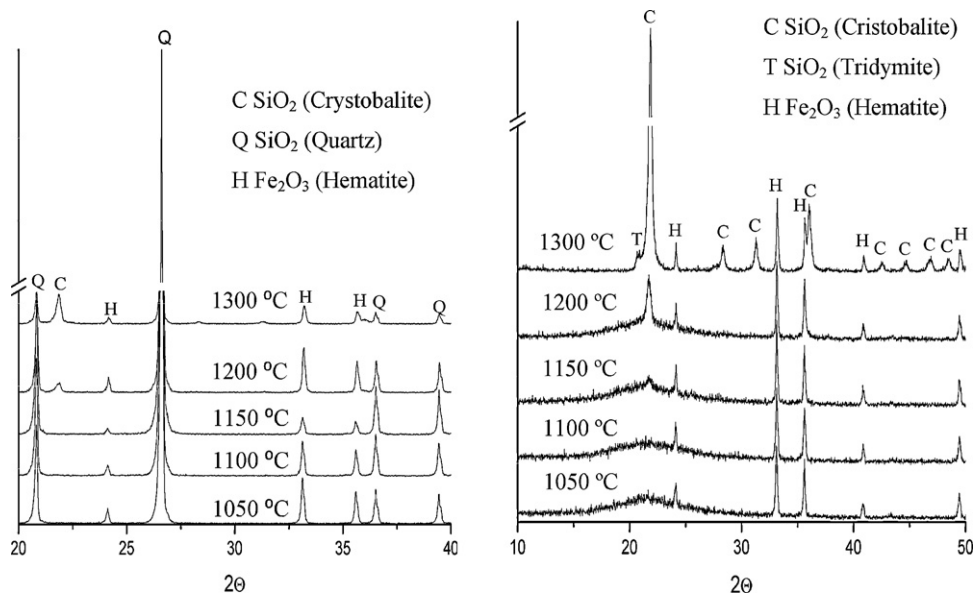
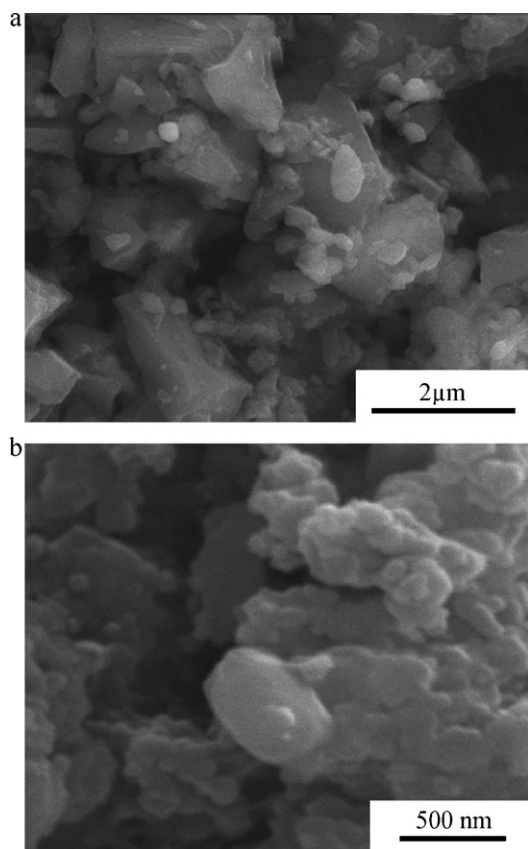


Fig. 4. XRD patterns of the temperature effect about the phases present in the material obtained from conventional milling content 15 wt% of hematite, fired at 1050–1300 °C. (a) Quartz matrix. (b) Amorphous matrix.



**Fig. 5.** SEM images of the effect of temperature in the sintering for pigment content 15 wt% of hematite, calcined at 1200 °C, using conventional milling. (a) Quartz matrix. (b) Amorphous matrix.

perature significantly contributes to the interaction between silica and hematite. Sintering can be observed regardless of the milling process. This is due the small size of the particles of silica and its amorphous form.

Upon visual evaluation of sintered pigments it could be observed that the pigments that were encapsulated in a quartz matrix showed lighter pink coloring with small differences in hue when the milling processes used was compared. The best results were obtained in amorphous silica matrix, which showed a more intense pink color. The pigments encapsulated in an amorphous silica matrix and calcined at 1200 °C showed a reddish color. All pigments showed variation of color saturation that was proportion to the percentage of chromophore present.

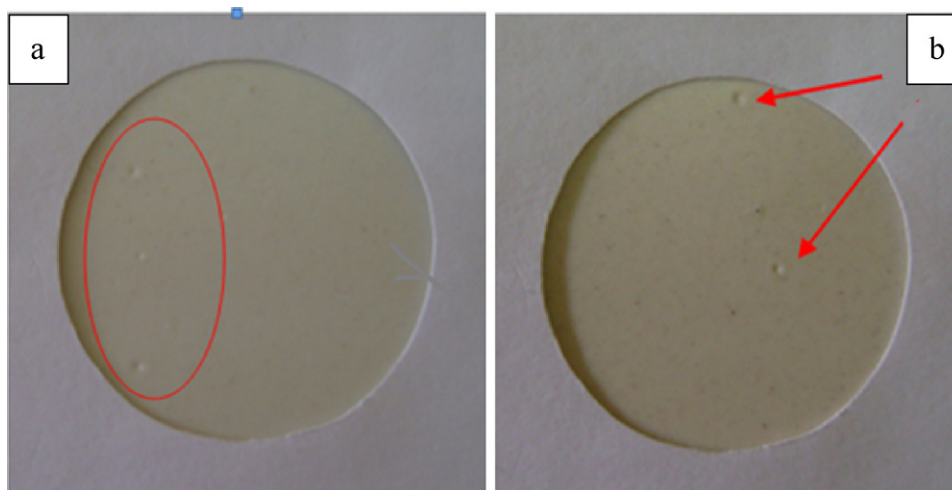
Upon the increase of the percentage of chromophore, all pigments showed variation of color saturation. The visual aspect of the pigment containing 15 wt% hematite and obtained after calcination 1050–1200 °C/2 h, for both matrices, is shown in Fig. 6.

Tests of color development in enamel pieces were made using white enamel. For formulations in a quartz matrix, the samples with low percentage of hematite added did not change the color of the enamel, regardless of the temperature used. Light yellowish hues were observed for samples with higher percentages of chromophore added and sintered at higher temperatures (1200–1300 °C/2 h).

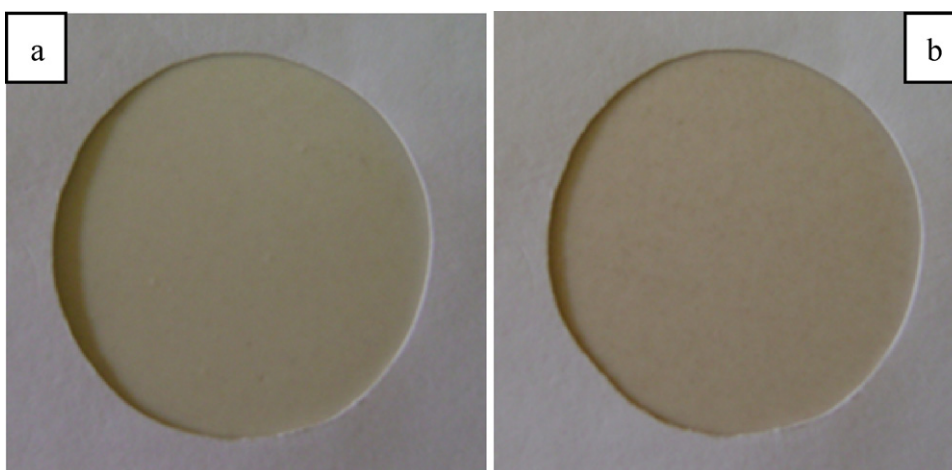
Samples with 15 wt% hematite added to the quartz matrix and mixed in high-energy mill showed surface defects, as evidenced by the two regions highlighted in Fig. 7. A similar behavior was observed for samples homogenized by conventional milling. The high size and dispersion of particles, does not enable the encapsulation process. A light pink hue could be observed when an amorphous matrix employing conventional milling was used (Fig. 8). This behavior was evident when a colorimetric analysis was performed. Only the enamel containing the pigment formulated with amorphous silica presented positive results for  $a^*$  param-



**Fig. 6.** Visual aspect of pigments (15 wt% of hematite) fired at 1050–1200 °C/2 h. CM, conventional milling; HE, high energy.



**Fig. 7.** Representative enameled samples: (a) Q15-AE-B and (b) Q15-AE-A. Q15, quartz matrix content 15 wt% of hematite; HE, high energy; B, pigment fired at 1050 °C/2 h; A, pigment fired at 1200 °C/2 h.



**Fig. 8.** Representative enameled samples: (a) Q15-MB-A and (b) A15-MB-A. Q15, quartz matrix content 15 wt% of hematite; A15, amorphous matrix content 15 wt% of hematite; MB, ball milling; A, pigment fired at 1200 °C/2 h.

ters. For the enamel containing pigment formulated with the quartz matrix, all samples had negative results for  $a^*$  parameters and high positive results for  $L^*$  parameters, regardless of the method of milling and temperature used, as seen in Table 3.

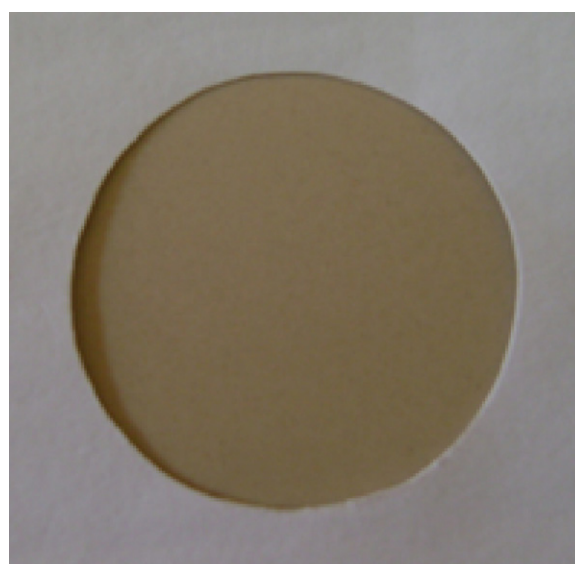
For application in porcelain body a standard technical porcelain piece was used (Fig. 9). An increase in the intensity of color proportional to the content of pigment added was observed for all applications made.

A difference in hue between the matrices used was also observed. Quartz and amorphous matrices showed intense brown and red coloration, respectively (Fig. 10). The formation of these coloring phases was also confirmed by colorimetric analysis (Table 4).

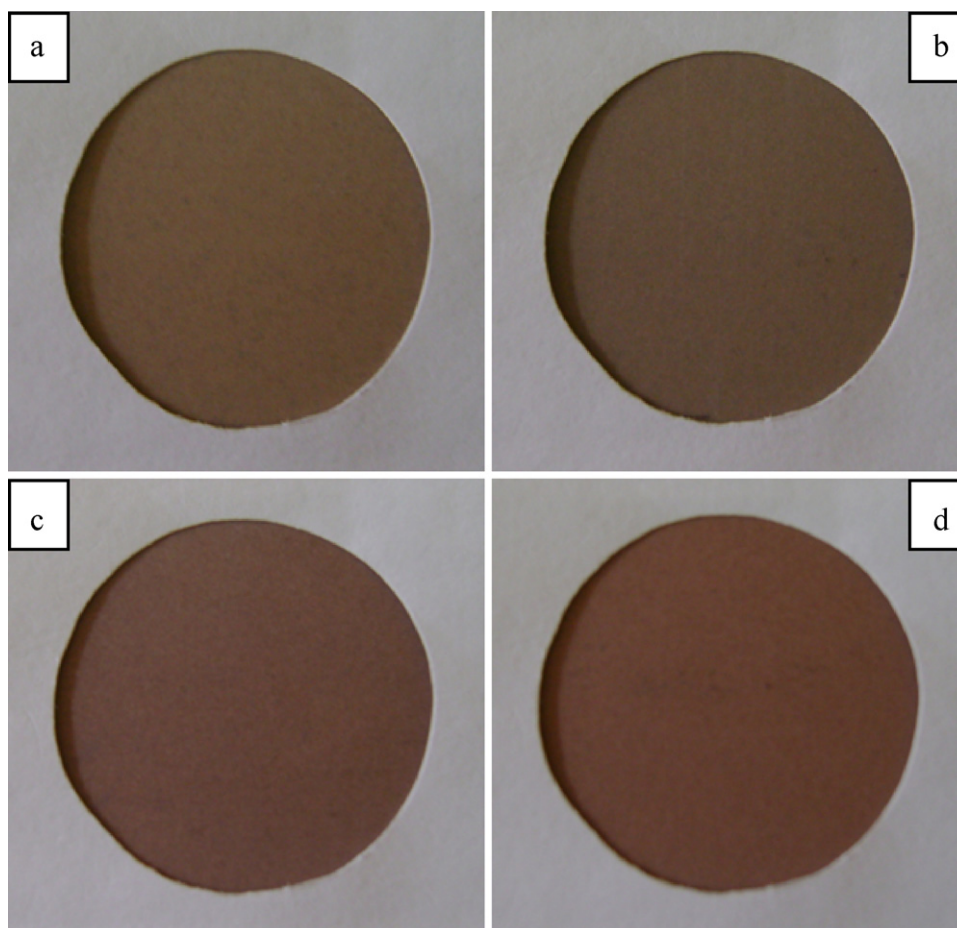
**Table 3**

Color parameters ( $L^*a^*b^*$ ) of the enameled representative samples. Q, quartz matrix; A, amorphous silica matrix; MB, ball mill; HE, high energy milling; B, pigment fired at 1050 °C/2 h; A, pigment fired at 1200 °C/2 h.

Enamel (15%)	$L^*$	$a^*$	$b^*$
Q15-AE-B	89.69	-1.13	7.63
Q15-AE-A	89.69	-0.81	7.69
Q15-MB-A	88.40	-0.85	7.99
A15-MB-A	85.37	0.86	-1.31



**Fig. 9.** Representative porcelain sample with pigment.



**Fig. 10.** Representative porcelain samples: (a) Q15-MB-A, (b) Q15-AE-A, (c) A15-MB-A and (d) A15-AE-A. Q15, quartz matrix content 15 wt% of hematite; A15, amorphous matrix content 15 wt% of hematite; MB, ball milling; HE, high energy; A, pigment fired at 1200 °C/2 h.

**Table 4**

Color parameters ( $L^*a^*b^*$ ) of the porcelain representative samples. Q, quartz matrix; A, amorphous silica matrix; MB, ball mill; HE, high energy milling; A, pigment fired at 1200 °C/2 h.

Porcelain (15 wt%)	$L^*$	$a^*$	$b^*$
Q15-MB-A	57.68	4.77	7.38
Q15-AE-A	60.63	5.32	7.53
A15-MB-A	54.31	7.48	5.77
A15-AE-A	57.26	8.03	7.53

However, it is important to highlight that the intense brown color existing in pigments homogenized in ball mills may be related to the presence of non-protected hematite particles, since this method of milling was less efficient. Nevertheless, the removal of non-protected hematite particles could result in lighter hues.

#### 4. Conclusion

The results showed that the percentage of chromophore added directly influenced the relative intensity of the peaks of hematite, and did not interfere with the crystalline phases: quartz to crystalline matrix and cristobalite to amorphous matrix. Also, there seems to be direct relationship between the temperature used in the synthesis of pigment and the effect of pigmentation.

The XRD patterns showed that when amorphous matrix is used an increase in temperature enables the formation of cristobalite and an increase in crystallinity. The relationship between temperature and pigmentation effect is associated with the formation of crys-

talline phases and the effect of encapsulation of the chromophore ion.

The results from the tests showed that the pigments used in a porcelain body developed a predominantly pink hue with a variation of saturation and brightness. However, the pigments that were encapsulated in both matrices, crystalline and amorphous, did not develop color when applied to enamel. This may be partly a result of the presence of zinc in the composition of ceramic glazes.

Thus, this study confirms that iron oxide from a metal sheet treatment process may be used as a ceramic pigment by encapsulation in a crystalline and amorphous silica matrix.

However, knowledge of properties such as content of chromophore added, the average diameter of particles and phases present is required.

#### Acknowledgements

The authors are thankful for the financial support from Capes, Portobello S/A for important contributions to this study and ArcelorMittal S/A and Endeka Ceramics Ltd for providing the samples.

#### References

- [1] S. Kumar, R. Kumar, A. Bandopadhyay, Innovative methodologies for the utilization of wastes from metallurgical and allied industries, Resources Conservation & Recycling (2006), doi:10.1016/j.resconrec.
- [2] M.A. Legodi, D. de Waal, The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste, Dyes and Pigments 74 (April) (2006) 161–168.

- [3] Y. Marinova, J.M. Hohemberger, E. Cordocillo, P. Escribano, J.B. Carda, Study of solid solutions, with perovskite structure, for application in the field of the ceramic pigments, *Journal of European Ceramic Society* 23 (213) (2003) e20.
- [4] D.M. Ferreira, S.R.H.M. Castanho, Incorporação de rejeitos sólidos galvânicos em vidros silicatos. Anais do 45<sup>o</sup> Brasileiro de Cerâmica. Florianópolis, SC, 2001.
- [5] K.W. Milanez, Incorporação de resíduo de galvanoplastia na produção de pigmentos inorgânicos. Dissertação – Universidade Federal de Santa Catarina, Florianópolis, 2003, 46 p.
- [6] V. Gomes, Desenvolvimento e caracterização de pigmentos cerâmicos baseados em alumina e mulita obtidos a partir de lama de anodização de alumínio. Tese – Universidade Federal de Santa Catarina, Florianópolis, 2005, 116 p.
- [7] G. Costa, V.P. Della, M.J. Ribeiro, A.P.N. Oliveira, G. Monroís, J.A. Labrincha, Synthesis of black ceramic pigments from secondary raw materials, *Dyes and Pigments* (2008) 1–8.
- [8] M.C. Casagrande, M.N. Sartora, V. Gomes, V.P. Della, D.A. Hotza, A.P.N. Oliveira, Reaproveitamento de resíduos sólidos industriais: processamento e aplicações no setor cerâmico, *Cerâmica Industrial* 13 (January/April (1/2)) (2008) 34–42.
- [9] M.A. Abreu, S.A. Toffoli, Reciclagem de resíduos sólidos industriais das indústrias automobilísticas e siderúrgicas como pigmento. Anais do 46<sup>o</sup> Brasileiro de Cerâmica, São Paulo, mai, 2002, pp. 1231–1292.
- [10] V.P. Della, Síntese e caracterização do pigmento cerâmico de hematita, obtida a partir de carepa de aço, encapsulada em sílica amorfa obtida a partir de casca de arroz. Tese – Universidade Federal de Santa Catarina, Florianópolis, 2005, 146 p.
- [11] A. Spinelli, A.P.N. Oliveira, L.E.B. Soledade, C.A. Passkocimas, E. Longo, A.G. Souza, C.A. Achicariano, J.A. Flores, Propriedades ópticas del pigmento  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, *Boletín de la Ceramic y vidrio* 44 (4) (2005) 223–227.
- [12] F. Bondioli, T. Manfredini, A.P.N. Oliveira, Pigmentos inorgânicos: projeto, produção e aplicação industrial, *Cerâmica Industrial* 3 (July/December) (1998) 4–6.