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Metallurgy dusts as a pigment for glazes and engobes

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ABSTRACT

This study is focused on using the dust from metallurgy as a pigment. The agglomerating dust is formed during metallurgical processes. This waste product is interesting for recycling process. The main mineralogical phase of dust is hematite α-Fe_2O_3. Both synthetic and natural iron oxides are commonly used as pigments in ceramic industry. In this experiment the metallurgy dusts were used as a pigment for preparation of glazes and engobes. Agglomerating dusts were used both precalcined thermally at 700 °C and 900 °C and in an original state. The prepared glazes were composed of a transparent glaze base with 10 wt% agglomerating dusts as pigment. The glazes calcined at 1060 °C were finally yellow colored and glazes calcined at 900 °C were brown colored. Engobes contained a ceramic clay base with 1, 5, 10 and 50 wt% of dust as pigment. Engobes calcined at 900 °C were red and grey colored. The pigments were characterized by X-ray diffraction (XRD), chemical (XRFS) analysis, granulometry (PSD), thermogravimetric (TG) and differential thermal (DTA) analysis, scanning electron microscopy (SEM) and CIELab values.

1. Introduction

Recycling of wastes is a current trend in all industrial fields. Products which are often termed as “waste” can be a good source of raw material and can have significant economic value. Reuse of waste materials can be regarded as an important factor in reducing of the consumption of natural sources. Many by-products with various quality and value are formed during iron and steel production. Recycling technologies allow a material recovery of these secondary raw materials with high iron content. The materials with high iron content are for example scales, blast furnace sludge, steelmaking sludge, and dusts. Some iron-rich waste can be reused in metallurgical aggregates; however, there are alternative uses for the remaining iron-waste. This limitation is caused by presence of some harmful impurities, primarily the content of heavy metals such as zinc and lead.

Agglomerating dusts are created in the form of solid particles during the iron and steel production and processing. These are carried by waste gases and captured by filters during the process of dry cleaning waste products in an agglomerating factory. About 75 kt of dust is produced annually in each factory. Most of this amount is destined to be recycled, but the challenge is that the different types of dust derived from waste product dry cleaning process have a different chemical composition. This study is focused on the dual possibilities of using agglomerating dust as a pigment for preparation of glaze and engobes versus the possibility of using that dust as an alternative source of dye for the ceramic industry on the other side.

Iron oxide is the most widespread natural pigment. Black and brown pigments are among the most important used in ceramic coatings. Besides the iron, black pigments may contain oxides of Co, Mn, Ni, Cu or Cr. The pigments are unstable for example in the presence of Mn oxide which can result in surface defects and unstable colour. In turn, pigments are defined as a compound, usually calcined, formed by colored metal oxides that are mixed with a glaze or pasta and form a uniform and colored ceramic tile. Among the possible coloring methods, due to technical or economic reasons, the most effective way is to achieve a stable colour by using pigments [1–4]. In general, the stability of pigment depends expect the chemical composition also on the crystal structure, respectively on the mineralogical composition. The reactivity of whole system is affected by the composition of input material. For example, salts and hydrated oxides decompose during the thermal processing, and they disrupt the crystal structure. This process increases the reactivity of the decomposed products as well as free radicals which are formed in the crystal structure and cause the desirable coloring of materials. The stability of the pigments, especially the stability of iron oxide pigment, does not depend only on size of particles but mainly on their shape, thus on the ratio of their length and width. The acicular shape of iron oxide particles is less suitable for the application, thus the ball shape of particles is preferred in most studies. Some iron pigments have limited stability during the thermal exposition, Table 1. In an oxygen atmosphere, the black pigment Fe_3O_4

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Table 1
Reaction equations for the production of iron oxide pigments [6].

Colour	Reaction	Process
red	2 Fe_3O_4+1/2O_2 → 3 α-Fe_2O_3	calcination
	2 FeO(OH) → Fe_2O_3+H_2O	calcination
brown	2 Fe_3O_4+1/2O_2 → 3 γ-Fe_2O_3	calcination

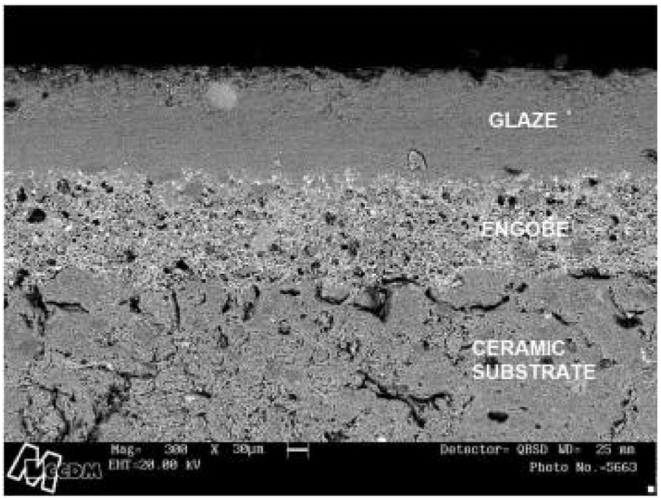

Fig. 1. Microscopic image showing the constitutive layers of ceramic tiles [7].

transforms at first to brown colour γ-Fe_2O_3 and later (above 350 °C) it modifies to red colour α-Fe_2O_3, which is stable up to 1200 °C in the air. Yellow colored iron oxide-hydroxide FeO(OH) decomposes above 180 °C to red colour α-Fe_2O_3, simultaneously with water removal. The thermal behaviour of brown iron oxides depends on their composition [5,6].

Pigment can be used for coloring of glaze and engobe. Glazed ceramics are always selected by their design and by their colour. Both factors represent the conditional parameter to obtain a colored glazed material whose characteristics are rarely determined by unique functional properties like hardness or strength. Engobe is interlayer applied between ceramic substrate and layer of glaze as shows Fig. 1. An engobe is applied for opacifying the substrate, to attenuate physical-chemical differences, to improve the fitting between the substrate and the glaze, and to reduce the defects on tile surface [7,8].

The focus of this work is the possible use of the agglomerating dust, a metallurgical by-product, as pigment for preparation of ceramic glazes and engobes. In this study, raw and calcined agglomerating dusts were used. The ceramic glazes were applied on porcelain tile surfaces by the spraying method. The engobes were prepared from brick clay and agglomerating dust and were applied on porcelain tile. Porcelain tiles with applied glazes were fired at 1060 °C/900 °C and substrates with engobes were fired at 900 °C. The agglomerating dust was characterized by chemical (XRFS) and crystalline phase (XRD) analysis, granulometry (PSD), surface area (BET), thermogravimetric (TG) and differential thermal (DTA) analyses, scanning electron microscopy (SEM) and CIELab values.

2. Experimental

Main raw material used for the experiment was agglomerating dust, in original dark avanturine (dark brown-red) colored, from agglomeration factory (Třineckéželezárny, a.s.). Agglomerating dust was used in both an original form (non-treated) and pre-calcined forms at 700 °C and 900 °C. Further raw materials were commercial transparent glaze (Glazura s.r.o.), brick clay for production of fired roof tiles, and ceramic slurry. The transparent glaze type P017 was used from (Glazura s.r.o, TORRECID GROUP, Czech Republic) which was modified using waste (agglomerating dust) as pigment. The transparent glaze is without any content of lead monoxide. The chemical composition of glaze is presented in Table 3. There were prepared the ceramic tiles as a substrate for application of glazes, which were calcinated at 900 °C. The substrate was porcelain tile. Transparent glaze was mixed with a) untreated agg. dust, b) agg. dust calcined at 700 °C, c) agg. dust calcined at 900 °C. The pigment was added to transparent glaze in amount of 10 wt%. Glazes were homogenized by wet method in laboratory ball mill for 20 min then were sieved < 0.2 mm. Glazes weight per litre reached value of 1570 g l^{-1}. The glazes were fired at the temperature of 1060 °C. The glazes are designed for the firing temperatures 980–1150 °C. It is possible to engrain the glaze using ceramic pigments. The parameters of thermal expansion of the body and the glaze were complementary. Glaze was applied by the method of spraying. Engobes were prepared from agglomerating dust and were added to both a) commercial brick clay for roof tile (after firing was red colour) and b) light ceramic slurry (after firing was light colour). Percentage of added dust was by amounts 1, 5, 10 and 50 wt%. Engobes were applied onto the surface of unfired ceramic body in amount of 0.7 g per 25 cm^2 of samples surface. Weight per litre was in the interval 1300–1350 g l^{-1}. Engobes were sieved < 0.2 mm and then were fired at the temperature of 900 °C.

The all samples were firing in an electric resistance furnace. The atmosphere in the furnace is oxidizing. It is a laboratory chambre furnace with heating from 5 sides including the bottom, protective SiC floor plates, and top insulating materials. Agglomerating dust was calcined at 900 °C for 3 h with 1 h stayed on maximum temperature. The colour glazed ceramic tile was fired at 1060 °C for 5 h with 1 h stayed at maximum temperature. Engobes were fired at 900 °C for 5 h

Table 2
Proportional representation of individual components in the glaze and engobe.

Samples	Substrate		Transparent glaze	Agglomerating dust	Temperature of firing of glazes and engobes	Temperature of calcination agg. dust
	brick clay wt%	ceramic slurry wt%	wt%	wt%	°C	°C
X1 / Y1[a]	–	100	100	10	1060/900	–
X2 / Y2	–	100	100	10	1060/900	700
X3 / Y3	–	100	100	10	1060/900	900
E01	100	–	40	1	1060	–
E02	100	–	40	5	1060	–
E03	100	–	40	10	1060	–
E04	100	–	40	50	1060	–
E05	–	100	40	1	1060	–
E06	–	100	40	5	1060	–
E07	–	100	40	10	1060	–

[a] X1- firing temp. of glaze 1060 °C, Y1 – firing temp. of glaze 900 °C, similarly also X2/Y2 a X3/Y3.