THE USE OF ELECTRIC ARC FURNACE DUST FROM STEEL RECYCLING IN CERAMIC GLAZE

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Abstract

Electric arc furnace dust (EAFD) is a waste from steel recycling in an electric arc furnace. Due to the waste mainly consisting of zinc ferrite along with a small amount of heavy metals such as lead and chromium, EAFD is categorized as a toxic waste. Even though proper treatments of EAFD offer crude zinc oxide and iron oxide, such appropriate EAFD recycling techniques have not yet been established in Thailand. The simplest way to reduce its toxicity is glassification. According to the EAFD's chemical composition, it is possible to use it as a raw material in decorative ceramic glazes which contain zinc and iron oxides. This project focuses on the possibility of using EAFD in ceramic glazes. The replacement of EAFD for common raw materials in Namako glaze was attempted. Its toxic release was tested by means of the toxicity characteristic leaching procedure. The results showed that the EAFD-bearing glaze was very similar to the traditional Namako. The obtained glaze provided non-crackle, deep blue, glossy surfaces with very small crystals. Heavy metal release, particularly lead, from the leaching test was lower than FDA standards, suggesting the proposed glaze was safe enough. This indicated that EAFD can be applied as an alternative material for ceramic glazing.

Keywords: Electric arc furnace dust, ceramic glaze, waste utilization

Introduction

Electric arc furnace dust (EAFD) is one of the wastes generated by the steelmaking industry. The waste is in the form of fine powder accompanied by fume gas during steel scrap melting in an electric arc furnace (EAF) and collected in the bag house for further treatments. Each ton of steel recycling provides approximately 15-20 kg of EAFD. According to a report (Iron and Steel Institute of Thailand, 2010) on Thailand's steel production from 2006-2010, the data showed that domestic steel recycling plants produced almost 100000 tons of EAFD each year and the amount of this waste tends to increase because steel scrap becomes the main raw material in steelmaking. In general, the dust contains 20-30% of zinc and 15-30 % of iron, which can be a potential resource of zinc and

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iron metals. The zinc content in the dust is significant and relatively high compared to that found in natural zinc ore (ZnS concentrates). The waste is mainly composed of stable zinc and iron complex oxides, so called zinc ferrite or franklinite ($ZnFe_2O_4$). The dust makeup also reveals several contaminants coming with steel scrap, for example phosphorus, chlorine, fluorine, silicon, manganese, copper, calcium, and aluminum. The contamination in the EAFD includes a small amount of some heavy metals, i.e. chromium, mercury, cadmium, and lead. Therefore, the EAFD is classified as a hazardous solid waste, 10 09 09 HM or, as a flue gas dust containing dangerous substances, K061. This leads to the incapability of EAFD being disposed of in landfills.

In fact, the zinc- and iron-bearing EAFD mineralogically and chemically provides many forms of oxide compounds which can be extracted from $ZnFe_2O_4$. The products include both crude and high purity zinc oxides, pig iron, and other more stable residues. However, the separation of zinc and iron from the EAFD requires proper techniques owing to the high stability of $ZnFe_2O_4$. pyrometallurgical processes (Juergen, 2007) such as the Waelz kiln, rotary hearth furnace, and plasma technologies, and hydrometallurgical processes (Guillaume *et al.*, 2008) like solvent extraction can be practically employed in many developed countries. Such state-of-the-art techniques must have cost-effective and highly efficient operating plants which crucially need to be strictly controlled in order to ensure that the EAFD treatments are undergone safely. In other words, there should be no further environment problems like dioxin emission in the case of pyrometallurgical methods or untreated solvents from hydrometallurgical treatments (Southwick, 2010). Unfortunately, no such EAFD recycling plants have been established or invested in yet in Thailand. To export the EAFD as raw material to the countries where recycling plants have worked properly or are already settled is still difficult due to environmental regulations and unclear government policy on EAFD handling (Iron and Steel Institute of Thailand, 2010).

A conventional and simple way to keep the toxicity of the EAFD at bay is glassification. EAFD is mixed homogeneously with silica-rich materials such as fly ash (Polsilapa and Wangyao, 2007), glass cullet, and silica sand (Pelino *et al.*, 2002), followed by being melted so that it becomes vitreous materials. The consequent products can be used as architectural bricks, concrete aggregates, roofing granules, abrasive grits, and glass ceramics (Jackson and Chapman, 1995). Owing to the EAFD's chemical composition, small amounts of many transition and heavy metals are also present. Lead in the dust offers magnificent fluxing property which is excellent for glass melting and several colouring agents are also restored. Therefore, the EAFD should be able to be used as a raw material for ceramic glazing. This work presents a deep blue decorative glaze made from EAFD and a commercial frit together with other typical glaze raw materials. The derived deep-blue crystalline glaze, so called Namako, is introduced. The EAFD is a replacement for zinc oxide (ZnO) and ferric oxide (Fe_2O_3). The glaze slip compositions were formulated and characterized. Heavy metal release from the products, especially lead, was also considered by means of leaching. The effects of the EAFD content on the glaze appearance were determined.

Materials and Methods

EAFD waste was collected from a domestic steelmaking plant (Kasemsakdi Co. Ltd., Thailand). The phase content, chemical composition, and morphology of the dust were characterized by X-ray diffractometry (XRD), x-ray fluorescence (XRF), and scanning electron microscopy (SEM) techniques, respectively. The particle size distribution was also detected by a laser scattering method. The dust was then mixed with other glazing ingredients, including a lead-free transparent frit (frit code 972, Ferro (Thailand) Co., Ltd., Saraburi, Thailand), Ranong kaolin clay, alumina, limestone, sodium feldspar, and potash feldspar. Carboxymethyl cellulose (CMC) and sodium tripolyphosphate (STPP) solutions were used as additives. As for the basic Namako glaze formula (Saiintawongsa, 2011), typical raw materials were used. Zinc and iron oxides were added up to 8 wt% and 10 wt%, respectively. With the addition of Fe_2O_3 3%, cobalt oxide ($C^{o}O$) 2%, and calcium fluoride (CaF_2) 5%, the Segar formula of this Namako glaze, with firing at 1230°C in an oxidation atmosphere, was as follows:

$0.2\ KNaO \quad 0.25\ Al_2O_3 \quad 3.0\ SiO_2$
$0.3\ ZnO$
$0.5\ CaO$

Adapted from the Namako glaze formula above, a non-lead containing transparent frit (frit code 972, Ferro Co. Ltd., Thailand) was used, the composition of which was higher than 10% of calcium oxide (CaO), around 2-10% of potassium oxide (K_2O), ZnO, barium oxide (BaO), and alumina (Al_2O_3) accompanied by a slight amount of magnesium oxide (MgO), sodium oxide (Na_2O), and boron oxide (B_2O_3). Both sodium feldspar and potash feldspar were still used as fluxing materials. CaF_2 was avoided and compensated for by calcium which existed in the dust. The glaze compositions were formulated using several raw materials as seen in Table 1. In order to investigate whether the dust can replace ZnO and Fe_2O_3 in a Namako glaze slip, the glaze T* represents the ingredient in which EAFD was a complete replacement for

Table 1. Composition makeup of the prepared glaze slips

Starting materials	Formulation of glaze slip (wt%)					
	STD	T1	T2	T3	T*	T4
Raw materials						
Zinc oxide (ZnO)	8.0	-	-	-	-	-
Limestone ($CaCO_3$)	17.0	17.0	17.0	17.0	17.0	17.0
Ranong clay (Al_2O_3•$2SiO_2$•$2H_2O$)	4.5	4.5	4.5	4.5	4.5	4.5
Flint (SiO_2)	28.0	28.0	28.0	28.0	28.0	28.0
Soda spar (Na_2O•Al_2O_3•$6SiO_2$)	18.0	18.0	18.0	18.0	18.0	18.0
Potash spar (K_2O•Al_2O_3•$6SiO_2$)	18.0	18.0	18.0	18.0	18.0	18.0
Frit code 975	6.5	6.5	6.5	6.5	6.5	6.5
EAF dust	**-**	***6.5***	***10***	***15***	***18***	***26***
Stain and Additives						
Iron oxide (Fe_2O_3)	10	-	-	-	-	-
Cobalt oxide (CoO)	2	2	2	2	2	2
STPP	0.08	0.08	0.08	0.08	0.08	0.08
CMC	0.07	0.07	0.07	0.07	0.07	0.07
Water	65	65	65	65	65	65
EAF dust : frit ratio (approx.)	n/a	1 : 1	1.5 : 1	2.5 : 1	3 : 1	4.5 : 1

all the zinc and iron oxide raw materials (approximate EAFD to frit ratio = 3:1). Other glaze slips containing different EAFD to frit ratios were also prepared, varying from 1:1, 1.5:1, 2.5:1, 3:1, to 4.5:1 and designated as T1, T2, T3, T*, and T4, respectively. All of the glaze ingredients were thoroughly blended and milled in a high speed ball mill with alumina milling media for 5 min. The specific gravity, viscosity, and % residue of the prepared glaze slips were carefully controlled. The specific gravity of the glaze slips fell between 1.3-1.5, while the viscosity or flowability of the slip was between 10-12 seconds, using a Ford cup (ASTM Standard D1200-10, (ASTM, 2010)). Then, the obtained glaze slip was applied over clay specimens (de-aired ball clay, Compound Clay Co., Ltd., Bangkok, Thailand) by spraying and fired at 1230°C for 30 min in air. The melting behavior due to various EAFD to frit ratios was observed. The melt fluidity of each glaze composition was identified by an inclined test. The appearance of the glaze, including color, glossiness, and defects like pinhole and cracks were monitored. As to its toxicity, the leaching test was carried out by means of the toxicity characteristic leaching procedures (TCLP) test method 1311 (United States EPA, 1992). The glaze composition with different EAFD to frit ratios was dry-mixed and then melted in crucibles. The molten glaze was cooled down and the EAFD-containing glaze was obtained. The derived EAFD frit was ground, screened, and put into the dilute acetic acid of pH 2.88. Using a rotary agitation apparatus with 30 rpm for 20 h, the frit residue was taken off from the solution. The availability of toxic metals in the dilute acid solution, particularly lead, was defined by inductively coupled plasma mass spectroscopy. Finally, the selected glaze slip was applied over the actual ceramic body.

Results and Discussion

EAFD Characterization

The chemical makeup of the EAF powders analyzed using XRF and XRD approaches are reported in Table 2 and Figure 1, respectively. Several elements were contained in the dust, however only a few of them were in significant amounts, i.e. zinc and iron. According to the type of steel recycling, most steel scrap and used iron products are galvanized to prevent corrosion. When they are recycled in an electric arc furnace, the off-gas and dust fume containing zinc are released and collected in the bag house. The gas and fume outlet comprises low meting point compounds and volatile substances including zinc oxide and lead which are considered to be hazardous. In the EAF powder used in this experiment, the amount of iron and zinc elements were about the same, 35 wt%, while lead was around 1 wt%. As far as the phase content (Figure 1) was concerned, franklinite ($ZnFe_2O_4$) and ZnO were detected as the main phases whereas

Table 2. Chemical analysis of the EAFD used in this experiment

Element	wt%	Element	wt%
Aluminium (Al)	0.24	Chromium (Cr)	0.53
Mangnesium (Mg)	1.51	Manganese (Mn)	2.67
Silicon (Si)	1.21	Zinc (Zn)	36.33
Chlorine (Cl)	9.77	Copper (Cu)	0.19
Potassium (K)	3.51	Lead (Pb)	1.74
Calcium (Ca)	5.59	Tin (Sn)	0.17
Iron (Fe)	35.77	Others	0.29

other peaks represented complex metal oxides. Other phases were not clearly characterized because they had too small amounts to be determined by the XRD technique, that is, less than 5 wt%. The morphological feature of the EAF powder is also illustrated (Figure 2). It was shown that the dust was quite irregular and agglomerated. The size distribution was bimodal and shifted due to particle accumulation. The median particle size (D50) according to a laser scattering method was around 26 µm. From the information in Table 2, it could be seen that the zinc-bearing dust mainly contained iron, lead, and other elements with even much lower content which are rather similar to fluxing materials, coloring agents, and additives which are used for ceramic glaze manufacturing procedures. In the ceramic glaze aspects, lead oxide (PbO) is a very strong fluxing agent while ZnO is a less strong flux. ZnO acts as a crystal former, an opacifier and becomes a coloring agent itself. ZnO and PbO can also promote vivid colors when coupled with other oxides, such as CoO. With a silica (SiO_2) source, ZnO itself can create structured strings or a macro crystalline structure of zinc silicates (Zn_2SiO_4). Meanwhile, a high Fe_2O_3 content combines with silica to form finer crystals in glaze, so-called aventurine. A combination of high zinc and iron oxide tends to give some kinds of crystals.

EAFD as a Glaze Ingredient

The preparation of the glaze slips was pursued in an ordinary procedure. Specific gravity of the obtained glaze slips was

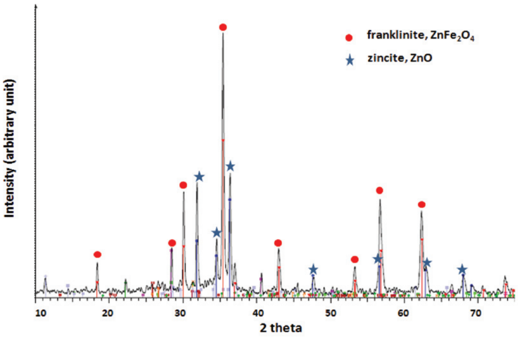

Figure 1. XRD patterns of the as-received EAFD powder

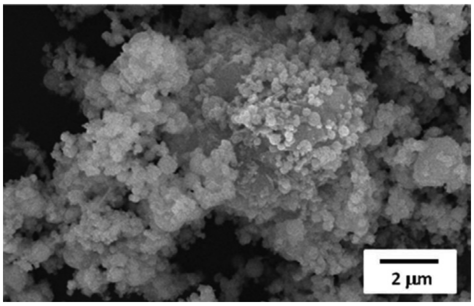

Figure 2. SEM of the EAFD particles

Table 3. Experimental results of heavy metal release and lead release allowance from FDA standards (SGS Consumer Testing Service, 2005)

glaze	dust: frit ratio	Heavy metal release (ppm)		
		Pb	Cd	Co
STD	n/a	n/a	n/a	n/a
T2	1.5:1	0.223	0.242	3.75
T3	2.5:1	0.253	0.236	2.88
T*	3:1	0.276	0.243	2.39
T4	4.5:1	0.239	0.242	2.64

Type of tablewares	FDA* (ppm)
flatware (plate)	3.0
small hollowwares (bowl)	2.0
large hollowwares (bowl)	1.0
cups and mugs	0.5
Large pitchers, jugs	0.5

** FDA = Food and Drug Adminstration, USA*

1.44 ± 0.03, while the slip viscosity was between 11.5 ± 0.8 sec. No residues were left in a sieve after being milled for 5 min. The melting behaviors of the EAFD in the glassy phase according to its content and temperatures were obtained (Figure 4). Only the frit and EAFD were mixed and pressed into a cone shape and then fired at various glaze firing temperatures. A transparent frit 972 was chosen to be a silica-rich material instead of milled silica sand in order to see the melting ability at 1100-1200°C. It was because of the fact that the frit was composed of SiO_2 with alkali and alkali earth oxides, and the mixtures were to be melted at lower temperatures compared to high purity SiO_2. When varying the fraction between the EAFD and frit, it could be seen that the more the frit fraction, the better the melting ability. For high EAFD contents, the cones could sustain their shapes, although the EAF powder contained lead and should have melted easily. They could not be collapsed at elevated temperatures since there were not enough SiO_2 sources to form any glassy phases, that is, merely 1 wt% of SiO_2 attached in the dust. Accompanied with alkali earth oxides in frit 972, the cones spread over more easily with higher frit contents at all temperatures. The cones started to melt in the frit to EAFD composition of 50:50 and so on. From Figure 4, the frit to EAFD fractions of 70:30

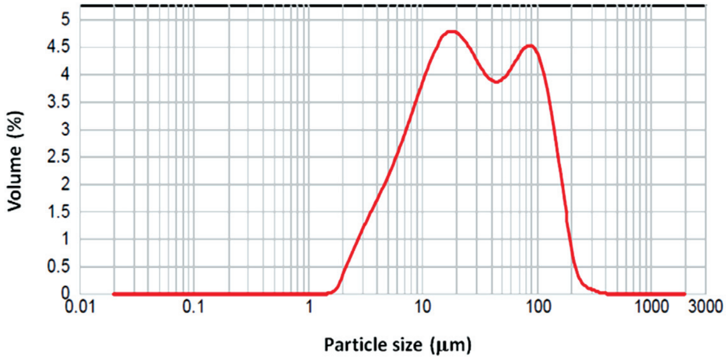

Figure 3. Particle size distribution of the EAFD powder

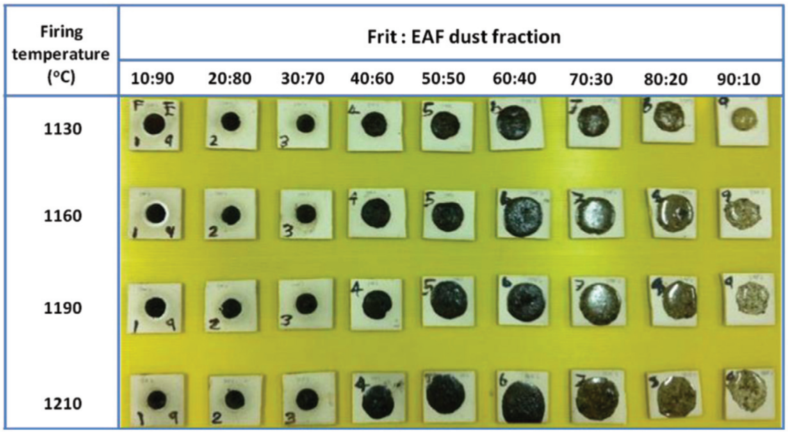

Figure 4. Melting behaviors of EAFD and frit 972 mixtures at various frit to EAFD fractions and at different firing temperatures

and 80:20 were likely to be the best ratios for melting. The optimum firing temperature was 1210°C, which was quite close to the temperature of the standard glaze recipe (1230°C), as reported in the literature (Saiintawongsa, 2011).

This work was concerned with whether, (1) EAFD could replace conventional raw materials and, (2) new glaze compositions containing EAFD were to be introduced. Above all, it had to be safe when glazed over ceramic bodies. Firstly, all ZnO and Fe_2O_3 in the standard glaze composition (STD) were completely replaced by the EAFD and the EAFD-containing glaze was denoted as T*. The STD and T* glazes were then fired and compared, as shown in Figure 5. Both glaze formulae provided relatively similar outcomes, blue, glossy surfaces with tiny crystals evenly distributed over the surfaces. A small amount of very fine pinholes might be seen in some T* specimens. The glaze could cover the ceramic specimens without any crawling or crackle surfaces. It was noted that the crawling defects found in T* (Figure 5 and Figure 6) were possibly caused by an improper coating technique, not by the glaze and body incompatibility. Therefore, it was clearly seen that EAFD could physically replace the traditional ZnO and Fe_2O_3. Secondly, the T* glaze was then formulated using various dust contents, extending to a broader spectrum from T*, of which the EAFD to frit ratio was 3:1, to others. Keeping the other basic ingredients, additives, and water constant, T1, T2, and T3 glazes were lower in dust content whereas that of T4 had an increased content (Table 1). The results are illustrated in Figure 6. A decrease in the EAFD amount led to dull and matt surfaces when compared with the STD and T* glaze. A deeper blue was presented and small crystals along with pinholes could be observed. In fact, the glaze was supposed to have a high melting ability due to the higher frit contents; in other words, it had less EAFD. Less EAFD reflected the lack of the fluxing agents, PbO, Fe_2O_3, and ZnO. ZnO generally reacts with CoO, generating a beautiful blue and PbO induces the glossiness and melting ability. PbO plays a role in both the melting nature as well as the flowability in a glaze mixture. Therefore, higher PbO from EAFD in a glaze mixture led to better melt flow, as seen in Figure 7, the inclined test. In the glaze T1 (ratio of 1:1), the color was deep-blue as a result of the CoO,

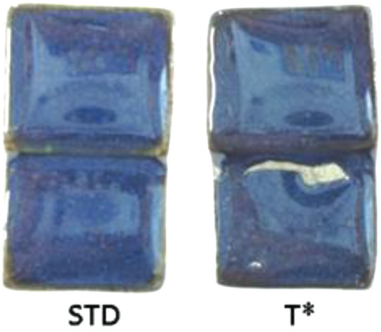

Figure 5. Blue, glossy-finish Namako glazes prepared from conventional raw materials (STD) and EAFD (T*)

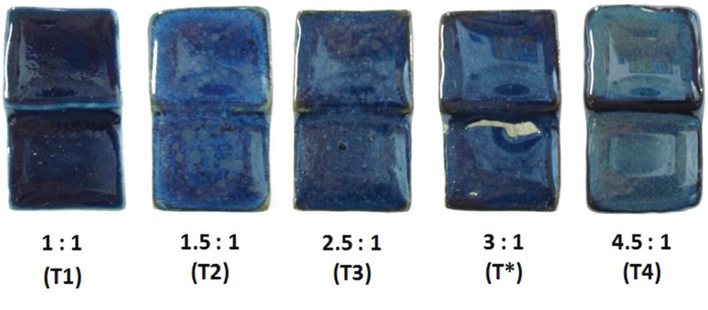

Figure 6. Appearances of the glazes prepared from various contents of EAFD (EAFD to frit ratios)

while the surfaces of glaze T2 (ratio of 1.5:1) and T3 (ratio of 2.5:1) were smoother and a bit brighter in colour. As for the T* (ratio of 3:1) and T4 (ratio of 4.5:1), the glaze textures were obviously more shiny and no pinholes occurred. The glaze T4, which held the highest amount of EAFD and resulted in a perfectly covered coating, slightly contradicted the results shown in Figure 4 but this might be explained by the PbO and SiO_2 relationship already mentioned previously. The shade of blue in T4 was also slightly paler relative to the T*. Therefore, the formulated T4 glaze was chosen to be coated over the actual bodies. Figure 8 showed a ceramic cup with a cylindrical contour which was applied with T4 and fired at 1230°C in air. The glaze perfectly covered the surface without any defects. It could be also noticed that the color displayed over the product had different shades from the top edge downwards to the bottom. It was black and a little bit matt at the top and then the color gradually turned brighter and become more bluish down to the lower part. The variation in colors is the typical nature of the Namako and could also be related to the thickness of the glaze. While firing, the glaze slowly flows down so the bottom area is expected to have a slightly thicker glaze layer than that of the top. This indicated that the appearance of the introduced T-series EAFD glazes might involve the thickness of the glaze.

Toxicity Testing

In order to use any solid waste as an alternative raw material, leaching of hazardous substances is crucially determined (Eun *et al.*, 2005). Lead can become a serious problem if released. The toxicity of the selected T4 was

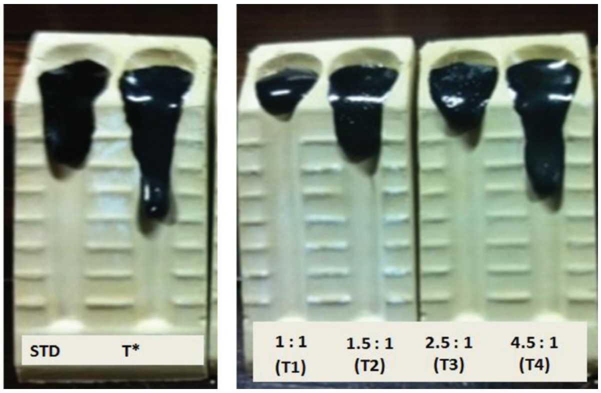

Figure 7. Inclined test of the STD Namako and the EAFD-containing glazes

Figure 8. Appearance of the introduced EAFD- bearing glaze (T4) on a cup

determined in order to ensure the glaze was safe from lead emission. From the TCLP analysis (Table 3), it was found that the values of lead release from all EAFD-bearing glaze compositions were acceptable when compared to the United States Food and Drug Administration (FDA) standards, which have been designed for food and drinks ceramic containers. However, the results were still higher than those of the Prop65 standards which are more restrictive than the FDA standards (SGS, 2005). The results revealed the release of cobalt and cadmium but their release was very limited. To guarantee safety, it was suggested that the glazes proposed by this research should be used only on decorative items.

Conclusions

The feasibility of using EAFD as a raw material in decorative glaze was investigated. Along with conventional starting raw materials, the glassified EAFD shows that it can be a substitute for both zinc oxide and iron oxide and offers a great potential as fluxing and coloring agents. New formulations of Namako containing the dust waste have been proposed. In comparison, the EAFD-bearing glaze tends to have better flowability and offer colorful bluish, glossy surfaces. The lead release test has been accomplished and the release is still acceptable. However, the EAFD is not recommended for food containers.

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