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Investigation of Possibility for Stabilization and Valorization of Electric Arc Furnace Dust and Glass From Electronic Waste

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Abstract:

This paper presents investigation of possibility for electric arc furnace dust (EAFD) and electronic waste (e-waste) valorization through stabilization process, in order to achieve concurrent management of these two serious ecological problems. EAFD is an inevitable waste material coming from the electric arc furnace steel production process, classified as a hazardous waste. Furthermore, it is well known that residual materials generated in the e-waste recycling process, like LCD (Liquid crystal displays) waste glass, are not suitable for landfill or incineration. In this study, these two materials were used for investigation of possibility for their valorization in ceramic industry. Thus, an innovative synergy of waste streams from metallurgical and e-waste recycling industry is presented. Investigation included a complex characterization of raw materials and their mixtures, using chemical methods, optical microscopy, scanning electron microscopy, as well as methods for determining the physical and mechanical properties. Based on these results, it was found that material suitable for use in ceramics industry as a partial substituent of quartzite and fluxing components can be produced. Besides solving the environmental problem related to EAFD and LCD disposal, by replacement of raw materials certain economic effects can be achieved.

Key words: EAFD, LCD glass, Solidification, Sintering, Ceramic materials.

1. Introduction

Electric arc furnace dust (EAFD) is an inevitable waste material generated in steel making process, where approximately 2% of the charge is converted into dust. Depending on the input material, fluxes or type of steel, the chemical composition of EAFD may vary significantly [1]. Generally EAFD is a complex, fine-grained material, particles size from 0.1 to 100 μm, containing high amounts of Zn and Fe as a main components, besides Ca, Mn, Mg, Pb and Cr and small quantities of Cd and As, and is classified as a hazardous waste why its disposal without treatment is forbidden [2, 3]. Despite the fact that EAFD cannot be disposed in regular landfills, due to economical reasons, worldwide recycling processes treats

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around 65% of EAFD, while the rest is still landfilled [4]. Generally, this kind of industrial waste can be treated either by pyrometallurgical or hydrometallurgical, or by combination of these two methods. However, finding the cost effective and environmentally friendly process for metals recovery from EAFD still represent a major challenge, due to insufficient zinc yield and its mineral form, as well as presence of various impurities in final products [5, 6].

However, presence of fluxing components, particularly alkalis, opens the possibility for valorization of EAFD in ceramics.

Worldwide, tremendous amounts of waste of electronic and electrical equipment (WEEE) are generated, of which modern TV sets and computer monitors represent a significant source [7]. In that manner, recent directives of European Union, like 2009/95/EC, are aimed on minimizing influence of hazardous substances contained within WEEE, signifying the importance of safe reuse, recycling and final disposal of waste equipment [8]. Liquid crystal displays (LCD) nowadays are widely used, but due to complexity of the process, only a part of discarded LCD monitors is being recycled. In the last several years, end-of-life LCD's are identified as a potential source for indium recovery, why various studies focused on indium recovery from discarded LCD's are reported [9-11]. However remaining solid material, LCD waste glass, is not suitable for landfill, incineration or composting [12]. Appreciable quantities and diversity of metallic materials and high content of SiO₂, Al₂O₃ and CaO indicate the possibility of valorization of these components in production of ceramics, but also synergistic effects in metallurgy [13].

According to available literature overview, different studies for EAFD and LCD treatment were reported, but all mainly focused on process of stabilization [14] and reutilization of the individual waste streams in asphalt mixtures [15], production of high grade materials [16], foamed glass [17] and as cement replacement [18]. Nevertheless, appropriate selection of materials combined for "disposal for the future", will allow highest possible degree of valuable materials recovering while minimizing wastes production. Therefore, the main goal of this study is development of the optimal technological procedure for stabilization and valorization of EAFD and LCD through conventional methods of synthesis and sintering, which will enable their transformation into inert materials suitable for use in ceramic industry.

2. Material and methods

2.1 Materials

Samples of EAFD were obtained from Serbian steel making company, equipped with electric arc furnace with capacity of 260,000 tons/year. The LCD waste glass was obtained from the local WEEE recycling company. Both raw materials were sieved on standard mesh type sieve in order to obtain $-100\mu\text{m}$ fraction and subsequently dried in laboratory oven at 105 °C for 24 hours. Prior to sieving and drying, raw materials were milled in a steel ball mill (Ø160mm, height 270mm, ball diameter 10mm, material + balls charge 60%) for 6h at 300min⁻¹.

2.2 Sample preparation

In order to investigate the possibility for EAFD-LCD stabilization and valorization using conventional methods of synthesis and thermal treatment, testing mixtures were prepared according to mixing matrix presented in Tab. I. As presented, six series with four different mixtures for each temperature were prepared providing a total of 24 mixtures. The dry homogenization of predefined quantities of EAFD and LCD glass was performed in an electric mixer. After homogenization, mixtures were compressed using two-sided uniaxial

pressing machine under pressure of 300 MPa, to form 32×13×10 mm cubic samples. Afterward, the pressed samples were heated to the temperatures of 600, 650, 700, 750, 800 and 900 °C, at a rate of 10 °C/min, in Marshall 9000 tube electro-resistant furnace. After reaching the defined temperature, samples were kept at constant temperature for 1 h, then cooled to 200°C in the furnace, and finally removed from the furnace to cool to room temperature.

In case of Series VI, samples sintered at 900 °C, 20 min after reaching defined temperature, started to melt, and were not used in further tests.

Tab. I EAFD and LCD glass mixing matrix.

Series	Sintering temp.	Sample No.	EAFD	LCD	Series	Sintering temp.	Sample No.	EAFD	LCD
			%					%	
I	600 °C	1.1	75.00	25.00	IV	750 °C	4.1	75.00	25.00
		1.2	68.75	31.25			4.2	68.75	31.25
		1.3	62.50	37.50			4.3	62.50	37.50
		1.4	55.00	45.00			4.4	55.00	45.00
II	650 °C	2.1	75.00	25.00	V	800 °C	5.1	75.00	25.00
		2.2	68.75	31.25			5.2	68.75	31.25
		2.3	62.50	37.50			5.3	62.50	37.50
		2.4	55.00	45.00			5.4	55.00	45.00
III	700 °C	3.1	75.00	25.00	VI	900 °C	6.1	75.00	25.00
		3.2	68.75	31.25			6.2	68.75	31.25
		3.3	62.50	37.50			6.3	62.50	37.50
		3.4	55.00	45.00			6.4	55.00	45.00

2.3 Analytical methods

Both, raw materials and sintered samples, were characterized in order to determine chemical and phase composition, morphology, mechanical properties, mass differences and heavy metals leaching degree. Chemical composition was analyzed by X-ray fluorescence (XRF, Thermo Scientific Niton analyzer) and atomic absorption spectrometry (AAS, Perkin Elmer 4000 spectrometer). Phase composition was analyzed using Jenapol U-Carl Zeiss polarizing microscope. Morphology of the sintered samples was analyzed by scanning electron microscopy (SEM) using JEOL JSM-5800 at 20 kV. Prior to the SEM analysis, samples were coated with gold using a sputter coater (POLARON SC502, Fisons Instruments). X-ray diffraction (XRD) analysis was performed using "Philips PW 1050" diffractometer. Cu-K α 1,2 radiation was used, measuring in 2 θ range 15-100°, step 0.02° and exposition 10s. Mechanical properties (compressive strength) of sintered samples were analyzed according to ASTM C1358-11 standard at servo tensile machine INSTRON 1332 with maximal load of 100 kN. Heavy metals leachability was tested according to the standard Toxicity characteristic leaching procedure (TCLP), US EPA method 1311 [19].

3. Results and discussion

3.1 Characterization of the raw materials

Chemical composition of raw EAFD and LCD glass is presented in Tab. II.

As presented, two major components of EAFD are Fe and Zn, in form of Fe₂O₃ and ZnO, partially bonded in form of ferrites (franklinite-ZnFe₂O₄). Among these two elements, significant presence of Ca, Si, Mg, Pb and alkalis was determined. Also significant presence

of Cl was determined, which ranges up to 1%. In case of LCD waste glass, major determined elements are Si, Ca and Al, while trace elements are Fe, Zn, Pb and Cu. Among all major and trace elements of EAFD and LCD waste glass, determined quantities of Pb, Cd and Cr in both materials, suggest on their toxicity.

Tab. II Chemical composition of raw EAFD and LCD glass.

<i>Element</i>	<i>EAFD, mass %</i>	<i>LCD glass, mas%</i>
Si (as SiO ₂)	4.89	47.31
Al (as Al ₂ O ₃)	0.27	6.29
Fe (as Fe ₂ O ₃)	25.37	0.85
Ca (as CaO)	6.5	3.66
Mg (as MgO)	7.93	0.95
Pb (as PbO)	3.79	7.91
Zn (as ZnO)	37.76	0.22
Mn (as MnO)	2.12	0.02
Sr (as SrO)	n.d.	7.60
Ba (as BaO)	n.d.	16.73
Na ₂ O	3.67	3.26
K ₂ O	2.56	4.66
S (as SO ₃)	2.74	0.12
C	1.08	n.d.
Cd	0.10	0.01
Cr	0.05	0.02
Cu	0.18	0.03
Cl	0.98	0.07
As	0.004	0.28

n.d. – not detected

Microstructure analysis of both raw materials was performed by XRD, SEM and optical microscopy. According to obtained results of the XRD analysis, presented on Fig. 1, dominant phases of raw EAFD are franklinite (ZnFe₂O₄) and magnetite (Fe₃O₄). Oxides of iron are also bonded with Ca and Mg in form of complex ferrites. Also, zinc is partially bonded in form of ZnO.

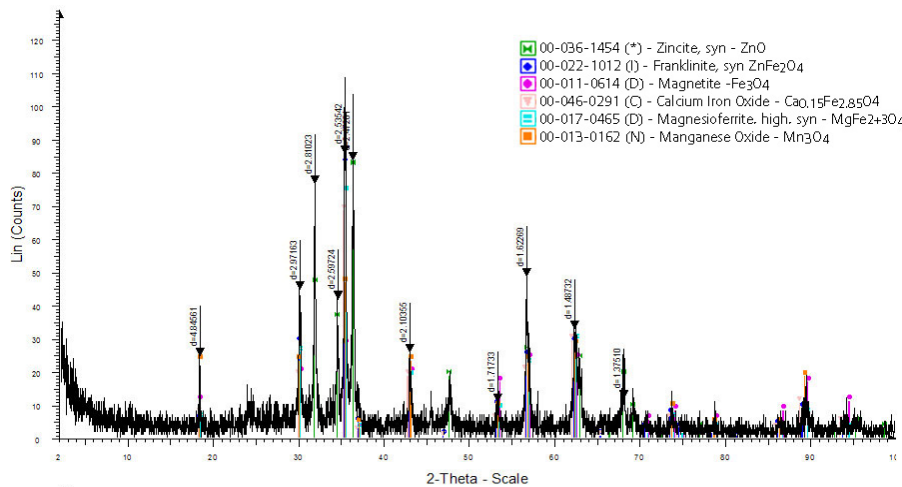


Fig. 1. XRD pattern of raw EAFD.

These results are confirmed through investigation of mineral composition by optical microscopy in reflected light. Generally, it was found that, due to the relatively small size but high surface area, EAFD is mainly composed of agglomerated particles of almost all phases, while appearance of individual phases is very rare. On higher magnification, using scanning electron microscopy, these particles were identified as spherical and flake-like forms of individual phases, Fig. 2(a). In case of LCD waste glass, SiO₂ was identified as major component, observed in form of small fractured particles, Fig. 2(b).

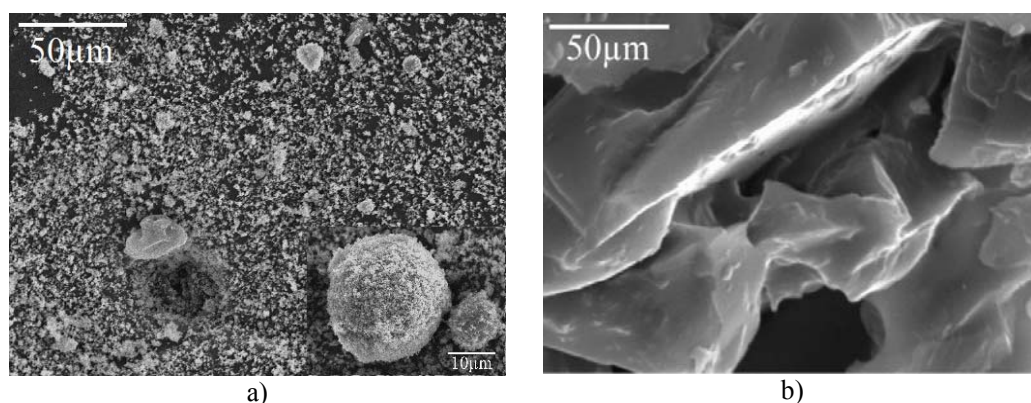


Fig. 2. SEM micrographs of raw EAFD (a) and LCD waste glass (b).

Results of heavy metals leachability from both raw materials are presented in Tab. III. According to obtained results, in case of LCD waste glass, heavy metals leaching degree is far below regulatory limits, while in case of EAFD, obtained results revealed that leaching degree of Pb and Cd exceeds regulatory limits.

Tab. III TCLP concentrations of raw EAFD and LCD waste glass.

Material	Cd (mg/l)	Cr (mg/l)	Pb (mg/l)	Zn (mg/l)
EAFD	18.1	<0.1	9.6	583
LCD waste glass	<0.05	<0.1	1.0	11
regulatory limits [19]	1	5	5	-

3.2 Characterization of EAFD-LCD mixtures

Determined chemical composition of EAFD-LCD mixtures was calculated to oxides content, and obtained results are presented in Tab. IV.

Tab. IV Chemical composition of EAFD-LCD mixtures.

EAFD/LCD	FeO	Fe ₂ O ₃	SiO ₂	CaO	ZnO	Fe _{tot.}
75/25	1.81	18.23	27.71	14.11	25.71	14.21
68.75/31.25	1.71	15.89	30.94	13.87	24.56	12.49
62.5/37.5	1.68	15.11	37.11	12.69	21.42	11.92
55/45	1.59	11.96	44.51	11.28	18.86	9.64

3.3 Characterization of sintered EAFD-LCD samples

Chemical composition of samples calculated to oxides content, sintered on border temperatures, 600°C and 800°C are shown in Tab. V. Depending on the sintering temperature,

volatile substances (VS) are in range from 3.17 to 6.12 and are referred to the evaporation of chloric and nitric compounds, as well on evaporation of ZnO.

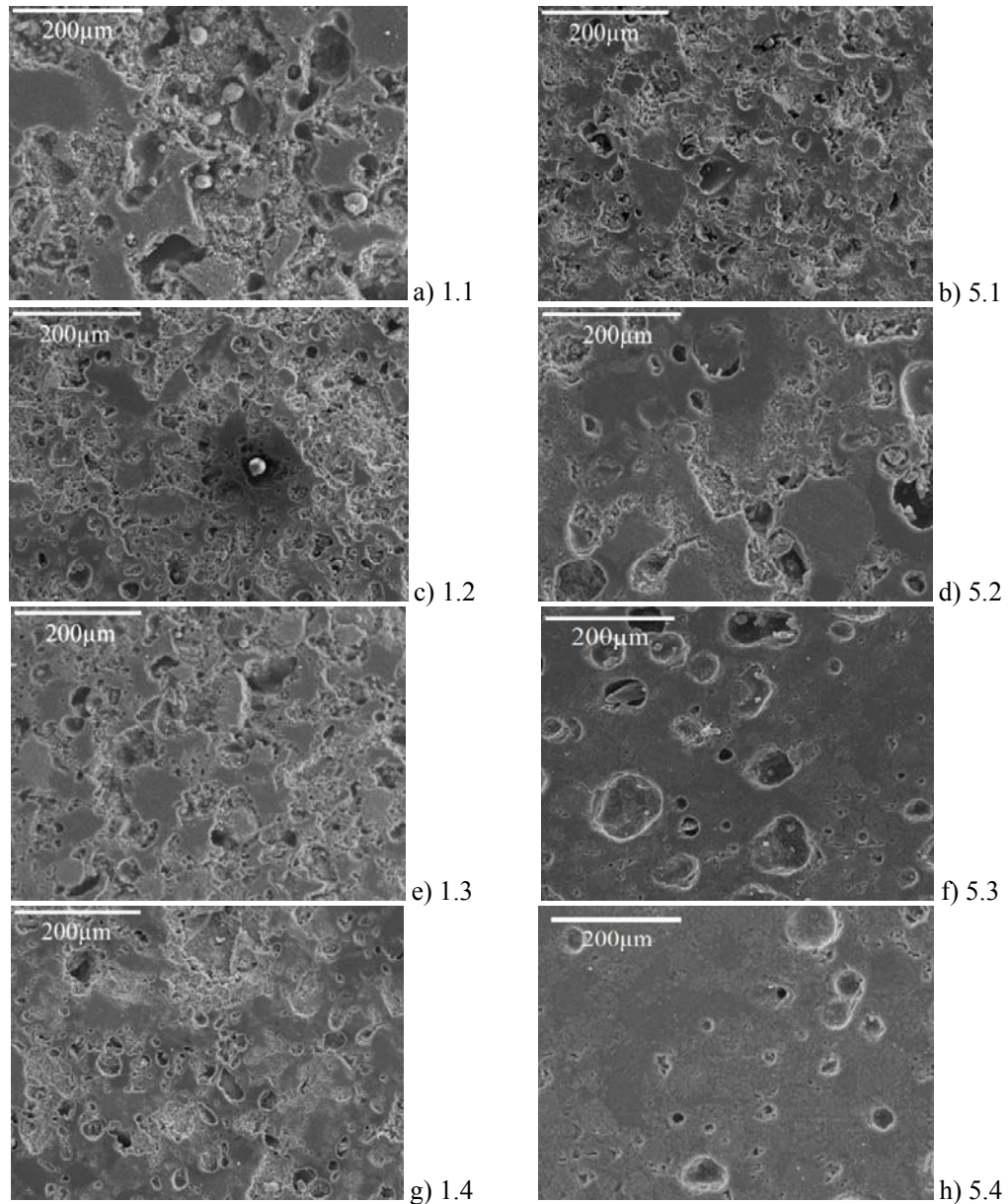


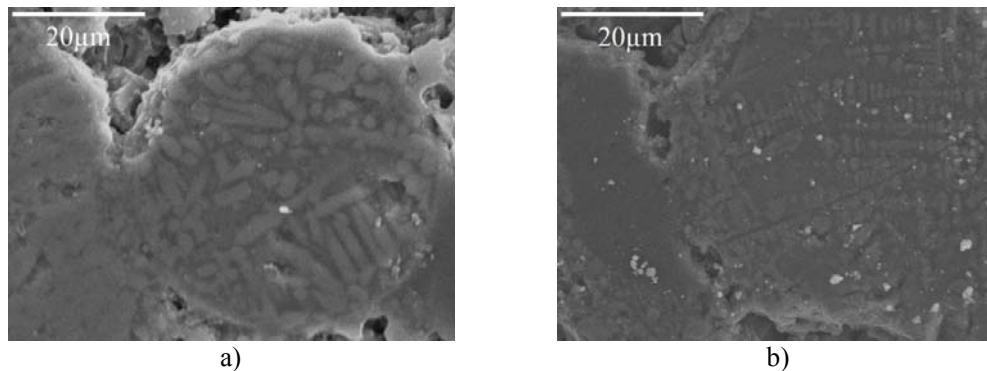
Fig. 3. SEM micrographs of sintered samples.

Results obtained by surface analysis at lower magnifications, of samples sintered at 600°C and 800°C, revealed structure typical for porous ceramic materials. As presented, Figs 3 a)-h), it is obvious that with the increase of EAFD overall porosity of the observed material increases. Furthermore, it was observed that with the increase of sintering temperature, apparent density decreases, as consequence of higher sintering degree.

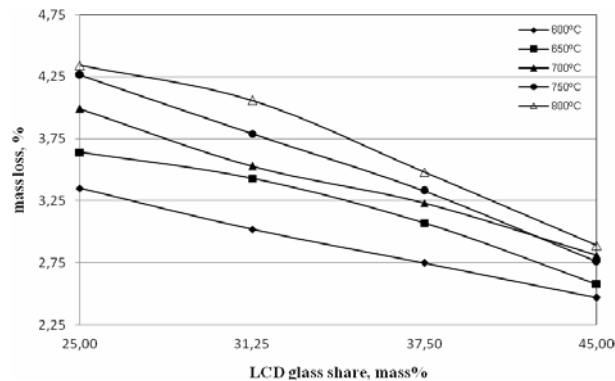
Tab. V Chemical composition of samples sintered on 600°C and 800°C.

Sample No.	Fe ₂ O ₃	SiO ₂	CaO	ZnO	VS	Fe _{tot.}
1.1	27.56	24.55	13.56	24.55	4.36	19.29
1.2	25.18	30.71	13.11	22.94	4.02	17.63
1.3	23.95	34.58	12.84	20.39	3.98	16.77
1.4	22.39	36.16	12.21	18.84	3.17	15.67
5.1	21.12	28.96	13.54	25.68	6.12	14.78
5.2	20.54	30.89	13.01	24.56	5.83	14.38
5.3	18.97	33.78	12.94	21.46	5.26	13.28
5.4	16.76	39.39	12.64	19.74	4.96	11.73

At higher magnifications, in almost all samples, identification of individual particles is very rare, yet, as a consequence of the conventional synthesis of EAFD and LCD glass, these particles are identified as agglomerates, which is typical for the reactions of solid state components during the sintering process. Nevertheless, these systems are characterized as less homogenous where it is not possible to control the stoichiometric ratio and grain growth and despite the fact that sintering was performed at temperatures below melting temperature, still certain degree of impregnation of phase with lower melting point (Ca ferrite) in solid phase of other component was observed, Fig. 4(a). Also, due to the local increase of reduction potential, sporadically isolated metallic droplets (Pb) were observed, Fig. 4(b).

**Fig. 4.** Extraction of Ca ferrite (a) and metallic Pb (b) in iron oxide basis.

Measurements of mass differences of all sintered samples revealed that weight loss generally increases with increase of sintering temperature. Due the fact that all volatile compounds, such are nitric and chloric compounds are present in EAFD, and are not contained in LCD, weight loss decrease with addition of LCD waste glass, Fig. 5.

**Fig. 5.** Weight loss of sintered samples.

As it is already determined, sintering temperature is closely related to development of porosity, i.e. material density differences, which finally results on mechanical properties of the material, particularly on compressive strength. Moreover, sintering at higher temperatures more positively impacts the compressive strength, as a high degree of densification was attained in the samples. As it was expected, obtained results, presented on Fig. 6, revealed that increasing of sintering temperature increases the strength of the treated material, particularly in case of decrease of EAFD, which is in accordance with results for chemical composition and sintering temperature influence on material density.

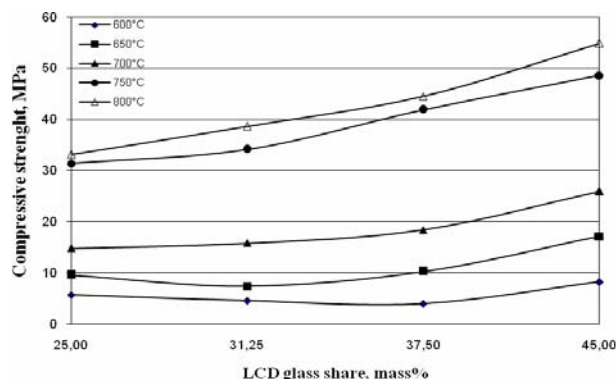


Fig. 6. Compressive strength of sintered samples.

Tab. VI TCLP concentrations of EAFD, LCD waste glass and sintered samples.

Sample No.	Cd (mg/l)	Cr (mg/l)	Pb (mg/l)	Zn (mg/l)
1.1	0.63	<0.1	3.1	258
1.2	0.67	<0.1	1.3	191
1.3	0.45	<0.1	2.2	152
1.4	0.67	<0.1	1.9	120
2.1	0.52	<0.1	3.2	157
2.2	0.49	<0.1	2.1	122
2.3	0.51	<0.1	2.3	148
2.4	0.29	<0.1	1.7	98
3.1	0.11	<0.1	3.4	73
3.2	0.09	<0.1	1.2	49
3.3	0.06	<0.1	4.1	114
3.4	0.41	<0.1	2.3	119
4.1	0.26	<0.1	2.4	109
4.2	0.14	<0.1	1.9	78
4.3	0.07	<0.1	1.8	86
4.4	0.11	<0.1	1.4	47
5.1	<0.05	<0.1	1.5	3.9
5.2	0.04	<0.1	1.4	51
5.3	<0.05	<0.1	1.3	4.6
5.4	0.93	<0.1	1.9	11
regulatory limits	1	5	5	-
Method	ISO 8288	ISO 8288	ISO 8288	SM 3111b

Although Cd, Cr and Pb leachability from raw LCD was very low and meet all regulatory limits, the amounts of these metals in EAFD, affected their leachability from testing mixtures. In Tab. VI, are presented results revealing that with applied procedure, stabilization of the material has been achieved, i.e. leachability of Cd, Cr and Pb is below regulatory limits in all samples, while in a case of Zn, although there are no regulatory limits, comparing to initial values of Zn leachability from raw materials, reduced leachability was observed.

4. Conclusions

Within presented work, through conventional method of synthesis and sintering of EAFD and LCD waste glass, their optimum ratio, in terms of mechanical properties and heavy metals leaching degree was determined, ensuring maximum stability of material suitable for use in the production of glass-ceramic materials as a partial substituent of quartzite and fluxing components, without compromising the quality of final products.

Comparing the raw material requirements in ceramic industry (it is estimated that world production is around 10^6 units of product/hour) production of EAFD and LCD waste glass is very low. In that manner, considering the characteristics of the synthesized and sintered material, based on EAFD and LCD glass, part of the fluxing components as well components used for improving the plasticity, could be replaced with this new material.

Using proposed process, addressing of a serious environmental problem arising from generated quantities of EAFD and LCD waste glass, together with certain economic benefits derived from partial raw material replacement, can be achieved.

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Садржај: У раду је приказана могућност валоризације филтерске прашине из електролучне пећи (ЕАФД) и електронског отпада (е-отпада), у индустрији грађевинске керамике кроз процес стабилизације, што представља истовремено решавање два озбиљна еколошка проблема. ЕАФД је обавезан пратилац електролучног процеса добијања челика, који је због својих физичко-хемијских карактеристика класификован као опасан отпад. Исто тако, позната је чињеница да остаци из процеса рециклаже електронског отпада, попут отпадног ЛЦД стакла, нису погодни за депоновање или спаљивање. У оквиру овог рада ова два материјала су представљала полазне сировине за испитивање могућности њихове примене у индустрији грађевинске керамике чиме је представљен иновативни приступ и синергетско дејство отпадних материјала из металургије гвозђа и челика и рециклаже е-отпада. Испитивања су обухватала комплексну карактеризацију полазних сировина, затим њихових синтетисаних синтерованих смеша, хемијским методама, оптичком микроскопијом, сканирајућом електронском микроскопијом, као и методама за утврђивање физичких и механичких карактеристика. На основу приказаних резултата утврђено је да се

конвенционалним начином синтезе полазних материјала, ЕАФД и ЛЦД, може добити материјал, погодан за примену у индустрији грађевинске керамике као сировина која може да супституише део кварцних и топитељских компоненти. На овај начин, поред решавања еколошког проблема депоновања ЕАФД и ЛЦД стакла, могу се постићи и извесни економски ефекти супституцијом природних сировина.

Кључне речи: ЕАФД, ЛЦД стакло, солидификација, синтеровање, керамички материјали.
