Structure Formation Processes and Green Ceramics Manufacturing from Hazardous Bauxite Red Mud and Ferrous Slag

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Abstract

This paper reports the development and characterization of some new ceramic materials from hazardous bauxite red mud (50 to 100 wt.%) and blast furnace slag (10 and 50%). This research aimed to demonstrate the possibility of expanding the raw material base for ceramics production, completely replacing the traditional natural raw materials (clay and sand) by hazardous industrial wastes composites with increasing local and global sustainability. Studies on the physicochemical processes of the ceramic structure's formation were conducted by the XRF, XRD, AAS, SEM with EDS, and LAMMA methods. Changes in flexural strength, linear shrinkage, water absorption, and density were determined during the sintering process at 1000°, 1050°, 1100°, 1150°, 1200°, and 1225°C. The ceramics' flexural strength after sintering at 1225°C reached 19.78 MPa due to the syntheses of the mainly glass-like structure formation, confirmed by SEM, EDS and isotopes LAMMA methods with the complete binding of the heavy metals.

Introduction

According to the authors of this paper, the best strategic way to hinder, or to delay as much as possible, the global ecological collapse, calculated and scientifically predicted by famous cosmologist S.W. Hawking [1], is the full usage of municipal and industrial wastes to replace traditional natural materials. He calculated that a further increase in the temperature of the atmosphere at the current pace will lead to the death of mankind in the next 300 years. It is well known that one of the largest atmospheric pollutants are dumps of industrial and municipal waste. From this it follows that scientifically based waste disposal is the main factor for the survival of humanity.

Bauxite processing waste, called red mud (RM), is a material that is produced when the Bayer process is applied to bauxite ore in order to obtain the aluminum oxide. According to the World Aluminum database [2], the world aluminum production summed 5,070 thousand metric tons in December 2017, which means that approximately 15 to 20 million tons of bauxite tailings were added to storage ponds worldwide. This large-scale production puts enormous pressure on the storage infrastructure of alumina refineries, which has caused some of the world's notorious catastrophes. For example, in 2010, the corner of an RM storage dam in Hungary [3] collapsed, and a wave of red mud flooded the streets of a neighboring city causing the deaths of ten people. The spill poured into the Danube and polluted 40 km² of land, contaminating the region's soil. High heavy metals content (Cd, Pb, Cu, Cr, Zn) and high pH of red mud (13) caused by the sodium oxide are two main reasons for its classification as hazardous industrial wastes. There have been a variety of similar accidents involving different types of tailings and mining waste. Two most recent of them in 2015 and 2019, were an iron ore tailings' overflow in Brazil [4]. The number of their victims is some hundreds of people, and the economic damage is several billions of dollars. These incidents illustrate that, even if advanced techniques are applied and storage is appropriately controlled, there is still a high risk of accidents.

The only way to prevent such catastrophes is to stop storing tailings and start recycling them completely as valuable raw materials. This paper presents scientifically based practical solution to the problem of hazardous RM application by using them in different composites with blast furnace slag (BFS) for production of environmentally clean ceramics.

According to [5], more than 1500 patents related to RM have been registered in patent databases around the world. However, [6] pointed out that one of the problems of RM recycling is that customers do not accept products made from waste materials, especially in case of bauxite tailings, which are hazardous waste material. The utilization of red mud in road bases and asphalt mixtures were reviewed and future research priorities were pointed out by [7]. Rychkov et al [8] intensified carbonate scandium leaching from bauxite red mud. It is possible to use red mud as adsorbent for enhancing ferricyanide removal [9]; or in mixes with fly ash to reduce CO₂ emissions [10].

The idea of employing it as a raw material for ceramics production is relatively common, being presented in different forms by researchers [11], who suggested mixtures of natural clay and RM, and investigated their optimal proportions. [12] prepared a solution of RM and fly ash as a foaming agent. [13] replaced 20% ordinary Portland cement by calcined red mud and hydrated lime without any loss of pozzolanic activity. [14] studied the role of Fe species in geopolymer synthesized from Bayer red mud; [15] treated red mud and cullet soda-glass at 600–800°C in order to synthesized foamed geopolymer with a compressive strength of 2.1–8.6 MPa. Singh et al [16] studied the influence of mechanical activation of red mud and curing methods on the strength of red mud - fly ash geopolymer paste. [17] presented a completely different approach to red mud recycling, where RM was treated as valuable material for further extraction of metals and other elements. The main flaw of this approach was that it led to the generation of more massive amounts of residue. The potential use of RM in cementitious materials' production was presented by [18]. Badanoiu et al [19] studied the role of Fe species in geopolymer synthesized from Bayer red mud treated red mud and cullet soda-glass at 600–800°C in order to synthesized foamed geopolymer with a compressive strength of 2.1–8.6 MPa. [16] studied the influence of mechanical activation of red mud and curing methods on the strength of red mud - fly ash geopolymer paste.

Because steel became a popular material long before aluminum, the blast furnace slag (BFS) of steel production already has some forms of implementation as a raw material. [20] used it for binding materials' production; [21] found that it was suitable as cementitious material from natural soils for road base construction to replace the two traditional layers of the base - sand and rubble - with a substantial increase in road strength. The blast furnace slag (BFS) was added to ceramic mixtures [22]; Bhardwaj and Kumar [23] replaced fine natural sand by slag as an aggregate material in concrete production.

The above review of scientific and technical literature shows the originality of our ceramic compositions consisting of only two types of hazardous industrial waste for the production of environmentally friendly ceramic materials.

Therefor the study had three main objectives: 1. to develop new environmentally friendly composites solely from hazardous industrial wastes, with particular emphasis on red mud (RM) and ground cooled

blast furnace slag (BFS), entirely replacing the traditional raw materials used in red ceramics manufacture - mixes of natural clay and sand (NC) - as an ecological alternative that presents suitable mechanical properties; 2. to develop ceramics which meet the requirements of the Brazilian standards on physical-mechanical and environmental properties; 3. to study the structure formation processes, responsible for the achievement of these properties of the ceramics.

The principal novelties of this study are experimentally proved three possibilities: 1. using red mud as a bonding component (instead of traditional natural clay) of the mixes with ferrous slag in all initial technological stages of ceramics' production - hydration of a homogenized mixes, compacting in a press, transfer and loading into a drying chamber and after that into a kiln; 2. at low temperatures red mud serves as a flux due to high soda content; the impact of slag as a flux is manifested at higher temperatures; 3. at the end of the ceramic firing process, all hazardous heavy metals are completely neutralized due to chemical interaction at high temperatures with other chemical elements of the initial mixes, or at least encapsulation in glassy structures of the ceramics. This the last phenomenon is the most valuable when utilization of hazardous industrial and municipal wastes and their transformation in an ecologically clean and safe state.

2. Methods And Materials

2.1 Methods

All the primary raw materials and the prepared ceramics were analyzed by various complementary methods. So, chemical analysis was conducted by XRF, using a PW 2400 Philips/Panalytical. XRD was performed with a PW 1830 Philips to identify the mineralogical composition. SEM photomicrographs were made using a Jeol JSM-6360 LV to determine the morphological structure of the particles. EDS analyses were carried out in a Jeol JSM-5410 LV to identify the microchemical composition of individual particles of the material. LAMMA was accomplished using a LAMMA-1000, X-ACT model to determine the isotopic composition. The solubility and lixiviation of metals from liquid acid extracts were investigated by AAS on a Perkin Elmer 4100 spectrometer; particles size distribution composition by a Laser Analyzer, model LA-950 – HORIBA. Three points of flexural strength were tested using an EMIC DL-10. Linear shrinkage, water absorption, and density were also studied.

The manufacture of the ceramic samples encompassed the following steps: mixing of the initial components according to the composition content (Table 1), addition of water (12–14%) to plasticize the mixes, compression of wet samples at 5 MPa in rectangular press-forms of 60 x 20 x 10mm size, drying to constant weight at 100°C, sintering for 3 hours (temperatures of 800°, 900°, 1000°, 1050°, 1100°, 1150°, 1200°, and 1225°C), and cooling by natural convection.

3 Research Results And Discussion

When performing these studies, both raw materials were studied, and after firing, the physical-mechanical properties of the developed ceramics and the processes of formation of their structures, explaining the properties obtained.

3.1 Raw materials characterization

Both raw materials were characterized in terms of their granulometric, chemical and mineral compositions and morphological microstructure, because these properties are the most effective on the structure and properties of the developed ceramics.

3.1.1 Chemical composition of the raw materials

Both industrial waste materials used as raw materials in the study were obtained from local factories in Brazil. The red mud (RM) was supplied by a refinery in Sao Paulo's state, and blast

furnace slag (BFS) from a metallurgical plant in Parana's state. The sample of natural clay mixed with 10% sand was obtained on the local ceramics production plant and was used with this work only as a generally accepted industrial standard.

Table 1
– Chemical composition of the raw materials.

Oxides	RM	BFS	CSM	Oxides	RM	BFS	CSM
Fe ₂ O ₃	29.9	62.1	6.1	Cr ₂ O ₃	< 0.1	0.3	< 0.1
SiO ₂	15.5	13.8	53.3	V ₂ O ₅	0.1	0.0	< 0.1
SO ₃	0.6	10.0	0.1	BaO	0.0	0.2	0.1
Al ₂ O ₃	21.2	2.6	24.7	P ₂ O ₅	0.0	0.1	0.0
CaO	4.2	2.5	0.4	SnO ₂	0.0	0.1	0.0
MgO	0.1	0.3	0.7	ZnO	< 0.1	0.1	< 0.1
Na ₂ O	10.3	0.9	0.1	CuO	0.0	0.1	0.0
K ₂ O	0.4	0.4	1.0	ZrO ₂	0.2	< 0.1	0.1
MnO	0.2	0.6	0.1	MoO ₃	0.0	< 0.1	0.0
TiO ₂	2.4	0.4	1.4	I.L.	14.4	1.7	11.5
P ₂ O ₅	0.6	3.5	0.1	Total	100.0	100.0	100.0

The main component of this research, red mud consisted mainly of Fe₂O₃ (29.9 %), followed by Al₂O₃ (21.2%), SiO₂ (15.5%), and Na₂O (10.3%), determined by the XRF method (Table 1). The rather high loss

on ignition value of the red mud (14.36%) might be explained by the carbonates content, by the hydroxide OH-group and the water content after undergoing the thermochemical Bayer process for bauxite ore treatment. The total Na₂O can be used as a good flux material, taking into account the low melting point of most of its forms. The presence in red mud of Zn (0.72%), Ni (1.26%), Ba (0.79%), Sn (1.18%) and Cr (0.54%) was also measured via the AAS method. These values far exceeded the relevant Brazilian norms [24]. The high pH value (13.5), with the high heavy metals content, forced to classify red mud as a hazardous waste. BFS contained extremely high amounts of ferrous oxides (63.6%) in addition to SiO₂ (13.8%) and SO₃ (10.0%), Al₂O₃ (2.6%), and CaO (2.5%). Natural clay with sand addition (NC), manufactured in local brick plants, was the only traditional raw material in the present study, used as a reference for industrial ceramics.

3.1.2 Particles size classification

The grain size classification (Table 2) showed that RM had a sum of particles from 0.3 to ≥ 1.2 mm equal to 85.46%. The majority of BFS particles (85.37%) on the contrary, presented sizes between 0 and 0.29mm. The RM showed high humidity (32.2%); DFS manifested no tendency to absorb water.

Table 2 - Grain size distribution in weight %, tapped density in g/cm³, and humidity (%) of the raw materials under study

Grain size distribution	Size (mm)	Red mud	Furnace slag	Clay-sand mix
	0–0.074	0.32	1.35	89.76
	0.075–0.149	1.08	17.63	5.68
	0.15–0.29	13.14	66.39	3.17
	0.3–0.59	46.13	14.63	1.39
	0.6–1.19	39.33	0.00	0
	≥ 1.2	0.00	0.00	0
	Tapped density (g/cm ³)	0.86	2.75	1.56
	Humidity (%)	32.2	3.1	9.34
*Tapped density refers to the bulk density of the powder after a specified compacting process, involving vessel vibration.				

3.1.3 Mineral compositions of the raw materials under study

The mineral compositions of the raw materials studied by the XRD method (Fig. 1) were also somewhat different: RM held magnetite Fe₃O₄, hematite Fe₂O₃, bauxite Al₂O₃·nH₂O, and quartz SiO₂, while BFS held

fayalite $\text{Fe}_2\cdot 2\text{SiO}_4$ and troilite Fe S .

All raw materials showed very weak crystal peaks and very robust X-Ray backgrounds due to the meager number of crystalline structures and the predominance of amorphous structures.

3.1.4 Morphological structures of the raw materials

Analysis of the particles' morphological structures (Fig. 3-a and b) suggested a wide variety of shapes, sizes, and forms of every material's grain, which meant there was no uniform structure. Such particle morphology indicated a predominantly amorphous structure of the materials, established by the XRD method. All of them were disconnected and had no chemical bonds between them. According to Table 1, Figs. 1 and 2, there was a significant difference between RM and BFS regarding chemical and mineralogical compositions and the structure of the particles.

3.2 Physical properties of the developed ceramics

The developed ceramics flexural resistance strength changes, linear shrinkage, water absorption, and apparent density after sintering at different temperatures were looked into to characterize their physical properties.

3.2.1 Flexural resistance strength of the developed ceramics

Red mud was the principal component of this study. It contained the remains of the alkaline

reagent from bauxite ore decomposition (hydroxide NaOH), having a melting point (T_m) of 323°C . This occurrence led to the formation of chemical compounds, such as NaHCO_3 ($T_m = 270^\circ\text{C}$), Na_2CO_3 ($T_m = 852^\circ$) and Na_2SO_4 ($T_m = 883^\circ\text{C}$). Therefore, these chemical species might serve as flux components during the ceramics firing process. The high content of these substances was a beneficial factor to reduce the firing temperature of the developed ceramics. For standard industrial glasses, the softening starts in the temperature range of $400\text{--}600^\circ\text{C}$ and ends between 700 and 750°C .

Comparing the flexural strength results (Table 3) obtained at $1,200^\circ\text{C}$ (12.17 MPa) and $1,225^\circ\text{C}$ (12.32 MPa), it may be stated that, at about $1,225^\circ\text{C}$, the RM was very close to the beginning of the excessive melting. An increase in BFS content drove to a decrease in the flux of RM content and an increment in the temperature of excessive melting of ceramics.

Table 3
– Flexural resistance strength of ceramics after sintering at different temperatures (°C).

Nº	Compositions, wt. %			Flexural strength (MPa) of ceramics sintered at T°C							
	CSM	RM	BFS	800	900	1,000	1,050	1,100	1,150	1,200	1,225
1	100	0	0	5.36	5.68	7.09	8.72	10.08	14.65	13.36	6.05
2	0	100	0	0	0	0.45	0.93	4.34	6.06	12.17	12.32
3	0	90	10	2.21	2.66	3.13	4.24	5.51	7.42	12.27	13.10
4	0	80	20	2.27	2.44	2.64	3.62	4.65	7.81	14.28	15.96
5	0	70	30	1.26	2.08	2.34	3.15	4.72	8.49	10.65	16.36
6	0	60	40	1.21	1.67	2.26	4.30	5.01	8.10	10.11	18.05
7	0	50	50	1.59	2.17	3.34	5.39	8.12	13.05	15.55	19.78

Therefore, ceramics 7, with the highest (50%) slag content, had the highest (19.78 MPa) strength after firing at 1,225°C, and ceramics 2 (without slag) and 3 (with 10% slag content) presented the lowest resistance (12.32 MPa and 13.10 MPa, respectively). According to the Brazilian standard [25], the flexural strength of solid bricks is classified as follows: Class A < 2.5 MPa; Class B from 2.5 to 4.0 MPa; and Class C > 4.0 MPa. That means, practically all developed ceramics corresponded to the demands of Class A (< 2.5 MPa) after firing at 800°C; to the demands of Class B (2.5–4.0 MPa) corresponded after 900°C the ceramics 3, and the ceramics 4 and 7 after 1,000°C and all other ceramics after 1,050°C; a class C corresponded ceramics 3, 6 and 7; after firing at 1,100°C all ceramics significantly exceeded the demands of class C (> 4.0 MPa).

The values of standard deviations of flexural resistance strength of the tested samples varied between 0.5 and 1.2 MPa.

3.2.2 Linear shrinkage, water absorption and apparent density of the developed ceramics

The changes in linear shrinkage values were studied (Table 4) by measuring the largest linear dimensions – samples' length - after sintering the samples at different temperatures (Fig. 3).

Table 4
Linear shrinkage (%) of ceramics at different temperatures (°C)

№	Composites, wt.%			Linear shrinkage (%) of ceramics sintered at T°C							
	NC	RM	BFS	800	900	1,000	1,050	1,100	1,150	1,200	1,225
1	100	0	0	5.36	5.68	7.76	9.09	10.47	11.52	11.95	11.86
2	0	100	0	1.89	2.27	3.42	4.33	5.29	7.24	11.67	12.45
3	0	90	10	0.96	1.08	1.92	2.98	4.30	5.64	9.43	9.56
4	0	80	20	0.54	0.63	0.81	1.51	2.64	4.41	7.40	11.07
5	0	70	30	0.07	0.24	0.31	0.83	2.46	4.38	11.37	12.54
6	0	60	40	0.04	0.11	0.18	0.39	1.69	5.26	12.32	12.35
7	0	50	50	0.08	0.12	0.17	0.44	1.13	4.28	10.99	11.40

In many cases, sharp changes were strongly linked to more significant changes in flexura strength. The linear shrinkage values increased up to a temperature of maximum strength. When the melting point of a sample was exceeded, the shrinkage decreased because of the foaming effect. The total shrinkage values of all compositions at all temperatures ranged from 0.04 to 12.54%. The values of standard deviations were between 0.4 and 1.7%.

3.2.3 Water absorption of the developed ceramics

The water absorption value (Table 5) is an indirect indicator of the porosity of the samples, so the changes in water absorption were also strongly linked to changes in their flexural strength.

Table 5
The water absorption value of the developed ceramics

№	Composites, wt.%			Water absorption (%) of ceramics sintered at T°C							
	CSM	RM	BFS	800	900	1,000	1,050	1,100	1,150	1,200	1,225
1	100	0	0	20.40	20.00	18.49	15.26	12.76	10.53	8.78	8.10
2	0	100	0	33.78	31.36	28.68	25.79	24.62	19.98	11.79	9.31
3	0	90	10	27.65	27.28	27.86	22.86	20.51	17.03	9.67	6.14
4	0	80	20	28.65	26.35	24.90	21.67	19.49	16.12	8.41	4.56
5	0	70	30	22.66	24.94	23.19	22.48	18.92	14.23	7.29	2.29
6	0	60	40	26.94	25.14	20.29	19.22	17.17	11.04	5.64	1.45
7	0	50	50	23.37	19.63	17.09	16.73	14.68	9.16	2.86	2.09

The water absorption values decreased with the temperature rise due to a more intense process of closure of the samples' open pores. The values decreased from and 35.22 to 1.35% with standard deviations values 0.07–2.1%.

3.2.4 Density of the developed ceramics

The nature of the changes in the samples' apparent density was similar (Table 5) to the changes in linear shrinkage values: they grew with the increase in temperature from 1.26 to 2.54 g/cm³.

Table 6
Density of ceramic composites after firing at different T°C

N°	Compositions, wt.%			Density (g/cm ³) of ceramics sintered at T°C							
	CSM	RM	BFS	800	900	1,000	1,050	1,100	1,150	1,200	1,225
1	100	0	0	1.56	1.58	1.61	1.70	1.77	1.84	1.87	1.80
2	0	100	0	1.28	1.31	1.35	1.42	1.44	1.55	1.89	1.96
3	0	90	10	1.38	1.42	1.47	1.50	1.56	1.62	1.82	1.87
4	0	80	20	1.47	1.52	1.55	1.58	1.65	1.72	1.99	2.16
5	0	70	30	1.53	1.59	1.64	1.62	1.72	1.81	2.26	2.47
6	0	60	40	1.71	1.75	1.77	1.77	1.82	1.97	2.24	2.54
7	0	50	50	1.85	1.88	1.90	1.90	1.96	2.14	2.40	2.51

Such behavior was highly expected, given the ongoing shrinkage of the samples and the reduction of water absorption (porosity) as the temperature increased. The values of standard deviations are within the limits of 0.09 and 0.4 g/cm³.

3.3 Physical-chemical processes of ceramics' structure formation.

Composition 7 was considered the most promising for the study of the physical-chemical processes of the ceramics structure formation for the following reasons: 1. the high content of red mud (50%); 2. the simplicity of its composition - only two components in a 50:50 ratio; 3. the very high flexural strength (8.12, 13.05, 15.55 and 19.78 MPa), corresponding to the demands of class C [25] (> 4.0 MPa) at the temperatures of 1,100°, 1,150°, 1,200° and 1,225°C correspondingly.

3.3.1. Changes in mineral composition during ceramics sintering

Comparison of the XRD patterns of ceramics composition sintered at 1,000° and 1,225°C (Fig. 4 and Table 7) revealed the presence of magnetite Fe_3O_4 , hematite Fe_2O_3 , fayalite Fe_2SiO_4 , albite $\text{NaAlSi}_3\text{O}_8$, and quartz SiO_2 , with a very high content of amorphous materials.

The vast majority of these peaks overlapped to one another. The only mineral peaks that were free from these simultaneities served as indicators of growth or reduction in the number of minerals formed during the temperature's rise from 1,000° to 1,225°C. A significant decrease in the only free peaks of fayalite at $2\theta^\circ = 34.2^\circ$ and the almost complete disappearance of hematite at $2\theta^\circ = 24.2^\circ$ were observed. It is well known that during sintering at high temperatures, hematite turns into magnetite. This transformation was not visible in Fig. 4 due to the absence of free magnetite peaks and their coincidence with hematite, fayalite, and quartz peaks, which suffered a decrease or even disappeared in Fig. 4-b.

Table 7
– Changes in position (d, Å) and intensities (I, %) of XRD peaks of Fig. 4, ceramic 7.

$2\theta^\circ$	Comp. 7 – 1,000°C			Comp. 7 – 1,225°C		
	d, Å	I, %	Symbol	d, Å	I, %	Symbol
23.9	3.7	53.74	H; A	3.7	28.46	H; A
24.2	3.67	36.73	H	3.6	8.37	H
26.6	3.3	11.57	Q			
33.2	2.69	100.0	H; A	2.69	100.00	H; A
34.2	2.62	15.53	F	2.62	5.17	F
35.7	2.51	68.89	M; H; F; A	2.51	56.76	M; H; F; A
40.9	2.20	21.34	F; A	2.20	17.64	F; A
42.2	2.14	3.84	A	2.16	8.86	A
49.6	1.837	28.13	H; F; A	1.838	23.33	H; F; A
54.2	1.692	33.51	H; F; A	1.691	28.12	H; F; A
57.6	1.598	6.61	H; F; A; Q	1.599	4.26	H; F; A
62.5	1.485	19.98	M; H; F; A	1.484	15.97	M; H; F; A
64.1	1.452	18.89	H; F; A; Q	1.452	13.68	H; F; A

The decrease in the intensity of almost all crystalline peaks of minerals was almost invisible to the naked eye, but it was neatly seen when comparing their intensity values in Table 7. The only mineral free of coincidence with other minerals' peaks was quartz ($2\theta^\circ = 26.6^\circ$), which disappeared after sintering at 1,225°C. Albite was the only mineral, which undoubtedly had its intensity increased ($2\theta^\circ = 42.2^\circ$). A

reduction in the intensity scale from 1,500 to near 1,400 counts per second also indicated a decrease in the number of crystalline phases in the ceramic, with its transition to the amorphous state.

3.3.2 Changes in the morphological structure during ceramics sintering

The comparison of SEM micro-images of the raw materials (Fig. 2-a and b) and ceramic 7 after sintering at 1,000°C and 1,225° (Fig. 2-c and d), at the same magnification (5,000 times), showed an increase in the particles' dimensions and their sphericity (Fig. 2-c) at 1,000°C, depicting the beginning of the initial mix's melting process. There were many pores of different sizes between the particles. Nevertheless, the flexural resistance value of the composite 7 (Table 4) increased until 8.12 MPa. The increase in the heating temperature up to 1,225°C showed (Fig. 2-d) a complete transformation of the earlier separated particles into a nearly pore-free glass-like monolithic structure. It seems the only explanation for the morphological changes might be the melting of all particles and the chemical interaction between them. Flexural strength enhanced almost 2.5 times, up to 19.78 MPa (Table 3) with significant improvement in other mechanical characteristics. The samples' edges of ceramics 7 (Fig. 3, the lowest) were slightly melted, and the surface turned black, apparently due to the transition of hematite to magnetite, which validated the XRD analysis' results (Fig. 4).

3.3.3 Microchemical composition of the ceramics' new formations.

The new formations were evaluated by the EDS method (Fig. 2d). Three different areas were analyzed, and all of them showed high heterogeneity (Table 8), such as Na content ranging from 0.00 to 7.16%, and Ca content from 0.00 to 7.00%.

Table 8
– The chemical composition of the points (Fig. 2d) by EDS method.

Spectrum	Na	Al	Si	Ca	Fe	Zr	Total
1	0.00	0.00	19.60	0.00	10.79	69.62	100.00
2	7.16	9.04	13.23	5.48	65.09	0.00	100.00
3	1.96	2.26	4.91	0.00	4.67	86.20	100.00
4	0.00	6.75	11.48	7.00	74.78	0.00	100.00
5	0.00	0.00	0.00	0.00	59.35	40.65	100.00
6	0.00	2.76	23.56	0.00	16.61	57.07	100.00

Similar results were obtained in isotopic compositions by the laser micro-mass analysis (LAMMA) method (Fig. 5).

The isotope sets (Fig. 5) and their percentage (peaks' height) exhibited a significant heterogeneity in their compositions at the comparable points.

3.3.4 Environmental characteristics of the developed ceramics.

The study of the leaching and solubility of the hazardous red mud extract showed that the heavy metals content (Zn, Ni, Ba, Sn, and Cr) far exceeded Brazilian toxicity standards [25]. For this reason, the ceramics of composition 7 were studied for leaching and solubility by the AAS method (Table 9). The comparison of these values before and after the use of red mud for ceramics production revealed a strong chemical fixation of heavy metals in red mud, culminating in more environment-friendly materials when compared with the requirements of the Brazilian norms [25].

Table 9
– Results of leaching and solubility tests of composition 7, sintered at 1,225°C.

Elements	Leaching, mg/L			Solubility, mg/L		
	Red mud	Comp. 7	[25]	Red mud	Comp. 7	[25]
As	7.63	0.21	1.0	9.56	< 0.001	0.01
Ba	94.28	< 0.1	70.0	95.47	< 0.1	0.7
Cd	7.34	< 0.005	0.5	15.41	< 0.005	0.005
Pb	4.43	< 0.01	1.0	7.66	< 0.01	0.01
Cr total	18.46	< 0.05	5.0	22.67	< 0.05	0.05
Hg	1.47	< 0.001	0.1	3.81	< 0.0002	0.001
Se	2.75	-	1.0	3.35	-	0.01
Al	28.76	< 0.10	*	36.44	< 0.10	0.2
Cu	16.29	< 0.05	*	30.08	< 0.05	2.0
Fe	98.31	0.07	*	108.75	< 0.05	0.3
Mn	55.11	-	*	69.43	-	0.1
Zn	68.48	< 0.10	*	84.13	< 0.10	5.0

According to leaching and solubility tests, the developed material presented no propensity to react with the environment. For this reason, ceramics might be shredded and recycled as an aggregate material in concrete's production at the end of their useful life.

Conclusion

It has been experimentally demonstrated that bauxite tailings might be used as the main component (up to a content of 80 wt.%) in composites with blast furnace slag. This study aimed to replace the traditional raw materials (natural clay) used to produce environment-friendly red ceramics with suitable mechanical properties.

The composition containing 50% of red mud and 50% of blast furnace slag showed almost 20 MPa of flexural strength, far exceeding the strength of ceramics made from traditional raw materials. It also presented low linear shrinkage (11.40%), low water absorption coefficients (1.95%), and moderate density (2.61g/cm³).

Physicochemical studies by XRD, SEM with EDX, and LAMMA microanalysis revealed that the new ceramics had mainly vitreous structures with small crystal inclusions.

Red mud held a high content of heavy metals, far exceeding the recommended levels of Brazilian sanitary standards. However, in the developed ceramics, all heavy metals were tightly bound in insoluble vitreous structures. Furthermore, solubility tests on the new ceramics showed their complete environmental compatibility. Therefore, the application of the suggested method on an industrial scale would have a positive impact on the ecosystems of industrial regions and cities. Firstly, preventing the disposal of hazardous waste, secondly, extending the service life of industrial landfills. Finally, decreasing the irreparable impact of quarries of traditional construction materials. At the end of the life span of the developed ceramics, they might be shredded and used as a filler for the production of concrete, because they remain utterly inert according to the leaching and solubility tests.

The materials developed might be highly profitable because the use of ordinary industrial waste products would significantly reduce the production cost compared to the relatively expensive traditional natural materials.

Declarations

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Availability of data and material – PhD thesis Kirill Alekseev and additional experiments

Code availability - PhD thesis of Kirill Alekseev

Authors' contributions

Vsévolod Mymrin - author of the idea, scientific supervisor of the study, developer of the plan of the experiments, participant of all research stages, first author of the manuscript

Kirill Alekseev – author of PhD thesis, principal researcher of all research stages

Rodrigo E. Catai - research participant, responsible for XRD analyses, co-author of the report and this manuscript

Walderson Klitzke – sinterização das amostras

Washington L. E. Magalhães - DTA and DRD analyses

Patricia R. Silva - DTA and DRD analyses, samples formation

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Figures

Figure 1

XRD patterns of the raw materials: a – red mud, b – blast furnace slag

Figure 2

Micro-structures of the RM (a), BFS (b) and composite 7 after sintering at $1,000^\circ$ (c) and $1,225^\circ\text{C}$ (d) with EDS analyses points

Figure 3

Photo of ceramics 7 after sintering at 1,225°C

Figure 4

XRD patterns of the ceramics of the composition 7 after sintering at 1,000°C (a) and 1,225°C (d)

Figure 5

Isotopes' laser micro-mass analysis (LAMMA) of the new formations of composition 7 after sintering at 1225°C