Hazardous spent methanol synthesis catalyst, bauxite red mud and ground cooled ferrous slag application to produce sustainable ceramics

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Abstract

New composites of sustainable ceramic composites from hazardous methanol synthesis catalyst waste, bauxite red mud and ground cooled ferrous slag were developed in this study. The ceramics were sintered at temperatures of 900°, 1000°, 1050°, 1100° and 1150°C for one hour. Almost all ceramic demonstrated fairly high properties, starting from a firing temperature of 1000°C. The best results were obtained after firing at 1050°C, which reached 25.98 MPa of flexural resistance, 8.80% of water absorption, 3.46 g/cm³ and 7.14% of linear shrinkage. Studies of physical – chemical processes of the ceramics' structure formation by XRD, SEM / EDS / mapping and LAMMA methods show the synthesis of mainly amorphous new formations with strong glass-like structures. Therefore, the result of leaching and solubility of the initial components' heavy metals in acid environment by the method of atom-absorption spectroscopy indicated their almost complete immobilization, which far exceeded the demands of Brazilian sanitary norms.

1 Introduction

Waste production has become a notorious problem in modern society. The degradation of the environment, the contamination of water and soil sources [1], and the eventual compromise of human health becomes evident. Studies refer to the possibility of using waste as alternative components in the manufacturing of different raw material, such as ceramics for civil construction [2]. According to Camargo, et al. [3], the sintering performs the encapsulation and stabilization of hazardous components to leaching. [4] point out that the reuse of residues harmful to health and the environment, transforming them into ceramic products, significantly reduces the impact of the industrial process.

Catalyst, according to [5], is a substance that increases the speed of a reaction without changing the Gibbs total energy variation. The world scientific and technical literature contains a lot of information about the use of various types of catalysts for a large number of very different catalytic processes. The catalysts used in the potential production routes are composed of metals such as cobalt (ethanol production), iron-copper-rubidium in the Fischer-Tropsch process (olefins, gasoline, paraffins and diesel) and copper-zinc-aluminum (methanol production) [6]. Recently, entropy stabilized catalytic systems have been raised great concerns due to the urgent demand for functional materials aiming to realize chemical catalysis [7]. Al-Faze, et al [8] studied dehydration of MeOH to dimethyl ether at the gas-solid interface in the presence of bulk and SiO₂-supported Keggin heteropoly acids. Luo, et al [9] provided an overview of recent processes in using in situ and operando spectroscopy to investigate the relationship between structure and activity/selectivity on oxide-supported metal catalysts and at metal-oxide interfaces. The catalytic oxidation kinetics of three chlorinated hydrocarbons as hazardous waste were determined by Manning [10] in an externally pumped recycle reactor with a commercially available chromia on alumina catalyst. However, the variants of methods for the disposal of waste from catalysis processes are not covered at all in the scientific and technical literature; this fact can only be explained by the absence of these methods.

Depending on the quality of the bauxite and the technical layout of the Bayer process, between 1.1 and 6.2 tons of red mud are generated per 1 ton of alumina produced. The cumulative stock of red mud in 2000 was around 600 million tons [11], in the world and almost 4 billion tons have already been accumulated till 2021 [12]. Therefore, it is “....one of the biggest challenges for the aluminum industry since its inception” due to “... the risk of releasing of waste into the environment” [13].

This official statement was confirmed by one of the most severe European ecological tragedies in Hungary 2010 with long-term ecological effects [14]. A million cubic meters of the red mud sludge of high alkalinity spilled from a reservoir at an alumina plant in Ajka; 10 people were killed, about 123 persons injured and 790 persons affected [15].

In order to utilize such a large amount of RM and to prevent the recurrence of such disasters, it is necessary to develop the maximum number of economically and environmentally attractive methods of disposal of this dangerous sludge. Therefore, several studies have been published on the use of RM for different purposes: as a catalyst [16]; for mine soil remediation [17]; for treatment of gold ores [17]; as an adsorbent for the removal of toxic pollutants [19]; as a pigment [20].

The study by [21], points out that the addition of 20% RM in clay promotes an ideal material for bricks manufacturing at 1050°C. [22] indicates that for the production of bricks, the addition of up to 50% RM sintered at 950 ° C for one hour, promotes compressive resistance superior to that found in material made only with clay. In a ceramic study, the influence of RM was analyzed by [23] on two different clay bases in the proportions of 0 to 50% of the waste.

Ferrous slag (FS) is by-product of metallurgical processes of pig iron and different types of steel melting. On average the production of one ton of steel results in average 300 kg of slag. Global steel production reaches 1870 Mt in 2019, approximately with 620 Mt of slag annual production [24]. In porcelain tiles, [25] developed samples containing more than 30% FS, obtaining flexural strength of up to 99.84 MPa. Even higher flexural resistance (110 MPa) of glass-ceramic composed of FS, quartz, sand and coal ash presented [26]. Other studies have shown that the use of ES is viable in cement incorporation Tsakiridis et al [27] and in use as an asphalt aggregate [28]. Mymrin [29] developed a new method of FS using as a binder for natural soils, as roads and airports bases material to replace conventional layers of sand and aggregates of natural rocks with very high economic and environmental efficiency.

[30] founded that up to 85% replacement of clinker by slag is possible without impairing strength of Portland slag cement. [31] mentioned that one of advantages of ground granulated blast furnace slag use is enhancement of the long-term compressive strength, especially after 40 days of curing. But [32], on the contrary, experimentally proved that strength and durability of mortars containing ground granulated blast furnace slag in acid and sulphate environment with slag is lower.

The main objectives of the present study were the following: 1. To develop new ceramics composites from methanol synthesis catalyst, bauxite red mud and ferrous slag without the incorporation of traditional natural raw materials (clay and sand) with enhanced physical-chemical characteristics in

comparison with Brazilian technical norms; 2. Reliably bind the heavy metals of the initial components of the raw materials to a level significantly lower than the requirements of sanitary standards of Brazil by carrying out the sufficient thermochemical reactions during the sintering of the developed ceramics.

2 Methods And Raw Materials Characterization

2.1 Methods

The initial industrial wastes, used as raw materials, and final ceramics, were studied by a complex of modern research methods. To determine the particle size distribution, the sieve method was used. The chemical composition was studied by XRF on a Philips/Panalytical, model PW 2400; the mineralogical composition – by XRD (Philips, model PW 1830, on $\lambda\text{Cu-K}\alpha$ and the High Score program with the PDF-2 database to interpret the diffractogram patterns). To study the changes of morphological structure was used method SEM (Jeol JSM-6360 LV). Micro-chemical analyses were conducted by EDS method (Jeol JSM-5410 LV). The isotope composition – by the laser micro-mass analyses (LAMMA) method (using a LAMMA-1000, model X-ACT). To study the level of chemical bonding of the chemical elements by the method of lixiviation and solubility in liquid acid environment was applied atomic absorption spectroscopy (FAAS or ICP-OES spectrometer).

The studies of the developed ceramics' mechanical properties changes after sintering at different temperatures were executed by method of three points flexural strength (by EMIC DL-10); water absorption of the ceramics – by the weight increase after 24 hours of their sample's total immersion in water; except, were determined density and linear shrinkage of the ceramics.

All three raw materials were dried at 100°C till the constant weight, homogenized in different percentages, with variations of 0 - 60% MSC, 20 - 40% RM and 0 - 40% FS and hydrated with water content 12-14%. The test samples were compacted at 5 MPa in a rectangular mold of 60 x 20 x 10mm in size, dried at 100°C till the constant weight, and burned for three hours at temperatures of 900°, 1000°, 1050°, 1100°, 1150°C, with a temperature increase speed of 10°C per minute, and with spontaneous furnace cooling.

The mechanical properties of the ceramics were replicated at five test samples with calculation of the average and standard deviation. The total quantity of the ceramics' test samples reached till 500 pieces.

2.2 Calculations

The study of the linear shrinkage LS (%) values was conducted in accordance with the equation:

$$LS = Li = [(Li - Ls) / Li] \times 100 \quad (1)$$

where Li - initial length of specimen (mm), and Ls - length of the specimen after the sintering (mm).

Water absorption coefficient (C_{WA}) tests were performed after ceramics' sintering by the following equation: $C_{WA} = [(M_{SAT} - M_D) / M_D] \times 100 \quad (2)$

where M_{SAT} - the mass of the test samples total water saturation during 24 hours, and M_D - the mass of the dry test specimen.

The values of density D (g / cm^3) were calculated by the equation:

$$D = M_d / a \cdot b \cdot c \quad (3)$$

M_d - weight of the dry sample after firing, a - length of the sample, b - width of the sample,

c - thickness of the sample.

3 Results

3.1 Raw materials characterization

Three types of industrial wastes - methanol synthesis catalyst (MSC), red mud (RM) from bauxite processing and ferrous slag (FS) - were used as the only raw materials components of the developed ceramics, completely replacing traditional raw materials (natural clay and sand).

The representative sample of RM was received from an aluminum factory in Sao Paulo; ferrous slag was obtained in the steel plant of the company Gerdau, in Curitiba. RM is a residue from the processing of bauxite, in the extraction of $Al(OH)_3$. The annually discarded mass of the MSC on the factory near Curitiba corresponds to forty tons of highly carbonized catalyst.

3.1.1 Particle size distribution of the raw materials.

All raw materials were crushed on a jaw crusher, dried till the constant weight at $100^\circ C$, milled in a ball mill and sieved on a sieve 1.14 mm. MSC in the form of cylindrical brilliant granules with a diameter of 0.55 cm and a height of 0.3 cm presented in the Fig. 1a and b.

The RM had 64.51% moisture, red color and homogeneous consistency. After grinding, the material has a major granulometry of ≤ 0.074 mm (72.67%). The ferrous slag (FS) after milling and magnet separation of molten iron particles contained almost all (98.65%) particle size between 0.59 - 0.075 mm with a major part of them (66.39%) had 0.29-0.15 mm size.

3.1.2 Chemical composition of the raw materials

The chemical composition of the MSC determined by RXF method (Table 1) mainly consists of copper oxide (58.2%), zinc oxide (24.0%), aluminum oxide (6.0%). The principal oxides of red mud are Fe_2O_3 (29.9%), Al_2O_3 (21.2%), SiO_2 (15.5%) and Na_2O (10.3%), total 76.9%. The ferrous slag mainly consisted of Fe_2O_3 (64.4%), SiO_2 (13.4%), SO_3 (9.7%), CaO (2.7%) and Al_2O_3 (2.5%). Some researcher [33, 34] rather informed similar chemical compositions of ferrous slag.

Table 1
Chemical composition of the raw materials (by XRF method)

Oxides	Compositions, wt. %			Oxides	Compositions, wt. %		
	MSC	RM	FS		MSC	RM	FS
SiO ₂	0	15.5	13.4	CaO	< 0.1	4.2	2.7
CuO	58.2	0	0.1	MgO	0	0.1	0.3
ZnO	24.0	< 0.1	0	TiO ₂	0	2.4	0.4
Al ₂ O ₃	6.0	21.2	2.5	P ₂ O ₅	2.0	0	0
SO ₃	0.3	0	9.7	BaO	0	0	0.2
Fe ₂ O ₃	0.1	29.9	64.4	Cl	0	0.2	0.3
Na ₂ O	0	10.3	0.8	Cr ₂ O ₃	0	< 0.1	0.3
K ₂ O	0.1	0.2	0.4	I.L.	11.3	14.4	0
Note: I.L. – Ignition Loss							

The high content of non-bonded chemical element in liquid extract of acid solutions was detected by AAS method. The results (Table 2) showed that leaching of all metals from flotation waste highly exceeded the demands of Brazilian standard sanitary norms [35]: As – in 5 times, Cr – 2.3 times, Cd – 9 times, Pb – 6 times, Hg – 22 times, Se -2 times.

Table 2 – Leaching and solubility of metals from red mud and composition 10 after sintering at 1150°C.

Chem. elements	Leaching, mg/L				Solubility, mg/L			
	MSC	Co.	Comp.	[35]	MSC	Comp.	Comp.	[35]
		9	10			9	10	
As	5.12	0.27	0.18	1.0	7.40	<0.001	<0.001	0.01
Cr total	11.29	0.86	1.26	5.0	18.53	0.02	0.01	0.05
Ba	79.13	0.86	1.22	70.0	82.15	0.02	0	0.7
Cd	4.35	0.09	0.13	0.5	9.22	0	0	0.005
Pb	6.19	0.10	0.15	1.0	8.06	<0.01	<0.01	0.01
Hg	2.17	0.12	0.05	0.1	3.11	<0.001	<0.001	0.001
Se	1.92	0.14	0.27	1.0	2.26	<0.001	<0.001	0.01
Al	2.16	0.11	0.19	*	5.13	0.11	0.04	0.2
Mn	3.55	0.14	0.08	*	5.21	0.07	0.02	0.1
Fe	23.47	0.43	0.73	*	29.16	0.1	0.04	0.3
Cu	7.72	0.07	0.04	*	8.28	0.49	0.25	2.0
Zn	6.38	0.04	0.08	*	7.45	0.76	0.54	5.0

A significantly more excess of hazardous chemical elements when comparing with the requirements of the same standards for the solubility of metals: Al - in 25 times, Mn – in 52 times, Fe - 97 times, Cu - 4 times, Zn – 1.5, As – 740, Cr – 371, Ba 117, Cd – 1844 times, Se – in 226 times.

3.1.3 Mineral composition of the raw materials

The XRD pattern of MSC (Fig. 2a) show the presence of the crystalline minerals melaconite (CuO), zincite (ZnO) and berlinite (AlPO₄) with rather high content of amorphous materials. The scale of the intensity of the peaks of crystalline structures of MSC almost reaches 1,500 count per second (l cps), which indicates the bigger quantity of crystalline structures compared to the other two wastes. The highest of them belongs to melaconite and berlinite.

Mineral composition of the bauxite treatment RM (Fig. 2b) is presented by rest of untreated bauxite Al₂O₃·xH₂O, hematite Fe₂O₃ and magnetite Fe₃O₄ and very small quantity of quartz SiO₂. Only two minerals' crystalline peaks at the angles of 2θ° = 18° and 26.5° have intensities near 700 cps due to coincidence of two minerals' peaks; all other peaks barely exceed the x-ray background line. That means the approximal equality of crystalline and amorphous phase in RM, or even the predominance of the amorphous phase over the crystalline.

Figure 2

The diffractogram patterns of the of the ferrous slag (Fig. 2c) demonstrate extremely low crystalline peaks (with I cps near 500) and the biggest contain of the amorphous materials. The crystalline materials presented by very small peaks of arsenopyrite (AsFeS), followed by chalcopyrite (CuFeS_2), pyrites (CuS_2) and quartz (SiO_2). Such a ratio of amorphous and crystalline phases should to lower the melting point of materials, if this will not be hindered by a high copper content (58.2%) in MSC with a sufficiently high melting point (1084°C).

3.1.4 Morphological structure of the raw materials

The analysis of the MSC sample by SEM method (Fig. 3a), in the magnifications at 5,000 times, presents cloudy conglomerates of irregularly shaped particles of different sizes from 1 to 4 μm with deep cracks, apparently due to grinding of the material. The RM sample (Fig. 3b) at the same 5000 times magnification is represented by even smaller particles from 1 to 2 μm .

These particles have a mainly rounded shapes characteristic typical for amorphous materials and are divided by pores also of various shapes and sizes. The degree of aggregation of these particles is much lower than that of MSC.

Figure 3

The ferrous slag particles after milling are presented (Fig. 3c) by the grains of 40 - 50 μm size, with a very dense monolithic structure, apparently due to slag melting in the metallurgical process. After milling the particles are covered by till 0.1 μm fine FS dust.

3.2 Mechanical properties of the developed ceramics

The values of flexural resistance, linear shrinkage, density and water absorption of the compositions submitted to sintering at 900° , 1000° , 1050° , 1100° and 1150°C were measured and discussed.

3.2.1 Flexural resistance of the developed ceramics

It is observed (Table 3) that the less flexural resistance at all sintering temperatures had the ceramics 1 and 2 with zero contents of MSC, 70 – 80% of red mud and 20 – 3% of slag. They continued also the strengthening process at 1100° , while all other ceramics were melted. The highest resistance (25.98 MPa at 1050°C) of the Table 3 at all temperatures had ceramics 10 with the biggest (70%) of MSC, 30% red mud and zero content of slag. The 10% decreasing of MSC till 60% with 40% red mud and with zero content of slag (ceramics 11) causes a resistance decrease at all temperatures. Particularly at 1050°C it was 13.05 MPa (twice less, than of the ceramic 10) and continued to gown up till 19.60 MPa at 1100° , in a contrary to ceramic 10, which resistance began to drop down till 13.97 MPa at 1100° because of the beginning of excessive melting at 1100° with complete melting at 1150°C .

The MSC substitution in the ceramics 11 by 10% red mud (ceramics 7) causes a strong decrease in the resistance of the ceramics at 1050° and 1100°C .

The following substitution in the ceramic 11 of 20% MSC by 20% of red mud (ceramic 5) leads to the proximity of the resistance values of the two compared materials, but is accompanied by a decrease in the melting point of ceramics 5 from 1100° to 1050°C.

All these facts clearly indicate the principal positive influence of MSC on the flexural resistance of the developed ceramics. The lowest melting point (between 1000° and 1050°C) had ceramic 4. A subsequent increase in the amount of red mud to 20% (ceramic 4) causes the maximum value of all ceramics (12.24 MPa) at 1000°C with almost complete melting of these samples at the following temperature 1050°C.

An increase in the content of red mud till 30% (ceramic 3) due to a decrease in the number of MSC leads to the lowest strength indices of samples, exceedingly only the ceramics 1 and 2.

Comparison of ceramics 3 resistance with two other ceramics 4 and 6 with the same 30% slag content confirmed once more the predominant effect of MSC on the resistance of materials: the highest values of resistance always belonged to ceramics 4 with the greatest (50%) of MSC.

The second resistance value in Table 3 belongs to ceramics 9 with only 40% MSC, but with 40% slag. Other ceramics with 40% slag content (ceramics 8) occupied the third place in resistance (19.12 MPa) at 1050, and at 1100°C it was completely melted.

As a preliminary brief conclusion, it can be said that the ceramics with the highest (70%) MSC content had the highest strength (25.98 MPa). The resistance values were close were ceramics with the maximum sum of MSC + FS = 40 + 40 = 80% (ceramics 9) or 30 + 40 = 70% (ceramics 8), significantly exceeding Brazilian standards' demands [36].

The presence of red mud in various quantities did not lead to very high strength values, but it significantly exceeded the requirements of Brazilian standards after sintering at 1000°C till melting. In addition, red mud reduced the melting temperature of ceramics: ceramics 4 between 1000° and 1050°C, ceramics 3, 5 and 8 between 1050° and 1100°C.

Table 3 - Flexural resistance of the developed ceramics after sintering at different temperatures.

Compositions (wt. %)				Flexural resistance (MPa) after sintering at T°C				
N°	MSC	RM	FS	900	1000	1050	1100	1150
1	0	70	30	0.98	1.99	2.34	4.57	6.99
2	0	80	20	1.05	2.06	2.39	4.66	7.91
3	40	30	30	0.53	4.25	8.02	6.13	Melt.
4	50	20	30	2.77	12.24	2.11	Melt	Melt.
5 -	40	40	20	1.94	9.33	13.52	6.25	Melt.
6	30	40	30	2.84	6.68	10.49	13.97	3.30
7-	50	40	10	1.30	9.22	10.28	14.40	2.83
8	30	30	40	2.47	5.79	19.12	Melt	Melt.
9	40	20	40	2.79	10.12	25.59	24.12	Melt.
10	70	30	0	1.29	10.02	25.98	13.97	Melt.
11	60	40	0	0.81	7.27	13.05	19.60	2.32

Note: Melt. – means complete melting of the test samples.

The standard deviation values of the flexural resistance from the obtained experimental data never exceeded 4% of the average means.

3.2.2 Linear shrinkage of the developed ceramics

The values of the linear shrinkage (LS) of the developed ceramics were increased with increasing of the sintering temperature (Table 4). The ceramics 1 and 2 with zero contents of MSC, especially in ceramics 2 with maximum (80%) of red mud had the less LS after sintering at all temperatures. This fact can be explained by their insignificant compaction during firing ongoing thermochemical processes of the component's interaction, which determines their low resistance (2.3 MPa) at 1100°C.

Table 4
– Linear shrinkage of the developed ceramics after sintering at different temperatures.

Composition (wt. %)				Linear shrinkage (%) after sintering at T°C				
N°	MSC	RM	FS	900	1000	1050	1100	1150
1	0	70	30	1.17	1.44	1.42	2.81	4.86
2	0	80	20	1.19	1.33	1.42	2.33	4.36
3	40	30	30	3.13	7.73	8.65	10.47	Melt.
4	50	20	30	3.36	7.68	8.14	Melt.	Melt.
5	40	40	20	3.30	10.19	11.83	13.83	Melt.
6	30	40	30	2.39	5.58	7.97	11.21	10.17
7	50	40	10	4.36	11.94	16.13	16.50	16.79
8	30	30	40	2.92	3.36	4.86	Melt.	Melt.
9	40	20	40	1.19	5.24	7.12	12.96	Melt.
10	70	30	0	5.67	15.00	17.14	17.63	Melt.
11	60	40	0	5.03	14.03	17.58	19.13	19.64

The ceramics 10 and 11, with zero ferrous slag content, had the maximum shrinkage values at all temperatures, which confirms the role of slag particles as a skeletal additive. Chemical composition of MSC includes 58.2% of Cu with melting point 1080°C and 24% of Zn with melting point 420°C (total 82.2%). During firing they produces well known alloy called brass with a melting point of 880° - 950°C, which depends on the percentage of these two metals. Exactly in this temperature range appeared an increase by 9 times in the flexural resistance of ceramic samples 10 and 11 (Table 3) and their linear shrinkage by 3 times (Table 4). The resulting brass can serve as a glue-like mass for 30-40% of the bauxite sludge of the ceramics 10 and 11, but also as a flux for its melting.

Therefore, the ceramics 8 and 9 with maximum (40%) slag contents had the minimum (after ceramics 1 and 2) shrinkage values also at all temperatures. They followed by the ceramics 3, 4 and 6 with 30% slag contents, which are higher than of the ceramics 8 and 9, but significantly less than ceramics 2 with 20% slag content. Shrinkage values closest to composition 10 and 11 are observed for ceramics 7 with 10% inclusion of slag.

The standard deviation values of the linear shrinkage were between 3 - 5%.

3.2.3 Apparent density of the ceramics after sintering

The density values of all compositions tended to decrease with increasing firing temperature due to faster weight loss compared with shrinkage samples. And only with excessive melting of the samples the density increased due to the filling of pores with the molten liquid phase and a sharp decrease in the volume of samples. Density values also depend on the percentage of components and mainly of the content of metals, such as Fe_2O_3 , CuO and ZnO .

The minimum values of apparent density (as the flexural resistance and linear shrinkage) had ceramics 1 and 2 with zero contents of catalysator waste. Ceramics 1 had a density slightly higher than ceramics 2 due to the higher ferrous slag content with 64.4% Fe_2O_3 compared with bauxite sludge (29.9%) Fe_2O_3 .

Table 5
– Apparent density of the developed ceramics after sintering

Composition (wt. %)				Density (g/cm ³) after sintering at T°C				
N°	MSC	RM	FS	900	1000	1050	1100	1150
1	0	70	30	1.73	1.70	1.67	1.73	1.82
2	0	80	20	1.64	1.57	1.55	1.65	1.71
3	40	30	30	1.92	2.04	2.30	Melt.	Melt.
4	50	20	30	2.26	2.62	2.64	3.24	Melt.
5	40	40	20	2.08	2.52	2.51	3.08	Melt.
6	30	40	30	2.12	2.25	2.32	2.53	3.09
7	50	40	10	1.95	2.45	2.45	2.37	2.76
8	30	30	40	2.12	2.20	2.29	2.44	2.83
9	40	20	40	2.25	2.47	3.00	3.14	3.42
10	70	30	0	2.44	2.63	3.46	Melt.	Melt.
11	60	40	0	1.99	2.60	2.98	3.27	3.44

The maximum density (3.46 g/cm³) after firing at all temperatures was found for ceramics 10 due to the highest content (70%) of MSC with 58.2% CuO and 24.0% ZnO and 30% red mud.

The standard deviation values of the apparent density never exceeded 0.3 g/cm³.

3.2.4 Water absorption (W_{ABS}) of the ceramics after sintering

The study of changes in water absorption is of great interest, since this characteristic is an indirect indicator of changes in the open porosity of materials. The value of W_{ABS} steadily changes with increasing temperature of ceramics sintering due to the formation of gases during 1. burnout of the

organics; 2. sulfur from a slag (9.7%) and MSC (0.3%), 3. the exit of water from the crystalline structure of bauxite $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (Fig. 2-B). Rather high values of Ignition Loss (I.L., Table 1) – 11.3% of MSC and 14.4% of RM - confirmed the inevitability of these reactions which are reasons for pores' formation when firing ceramics. But there is still a fourth reason, most effective and difficult to calculate: 4. gases of the thermo-chemical interaction of the components' mixtures.

Table 6 - Water absorption (W_{ABS}) of the developed ceramics

	Composition (wt. %)				Water absorption, (%) after sintering at T °C				
N°	MSC	RM	FS	900	1000	1050	1100	1150	
1	0	70	30	26.84	25.59	24.11	20.61	18.75	
2	0	80	20	27.67	26.24	25.83	21.40	18.58	
3	40	30	30	21.17	14.58	10.68	3.17	Melt.	
4	50	20	30	16.69	14.51	10.76	Melt.	Melt.	
5 -	40	40	20	20.79	10.21	10.46	3.18	Melt.	
6	30	40	30	18.16	13.62	11.03	8.79	4.30	
7-	50	40	10	22.94	13.88	9.13	6.29	5.91	
8	30	30	40	14.50	12.85	10.66	Melt.	Melt.	
9	40	20	40	13.26	10.74	8.62	6.58	Melt.	
10	70	30	0	23.12	11.47	7.65	6.44	Melt.	
11	60	40	0	24.08	13.56	8.05	4.87	3.39	

The highest values of W_{ABS} belonged to ceramics 1 and 2 with 70% and 80% red mud of bauxite processing and 20% slag, which is the best explanation of so low characteristics of these two ceramics. Ceramics 10 and 11 had the lowest W_{ABS} values at all temperatures prior to the start of excess melting at 1050°C due to the maximal (70% and 60%) of MSC contents.

The values of standard deviation of water absorption of ceramics after sintering at all temperatures no exceeded 0.4%.

3.3 Physical-chemical processes of structure formation of the developed ceramics

To study the physical-chemical processes of structure formation of the ceramics, two compositions were selected - 9 and 10; both of them demonstrates the best resistance (Table 3) before the beginning of the excessive melting, the highest apparent density (Table 5) and the lowest water absorption (Table 6).

Except, they have very different compositions of the raw materials and therefore different chemical and mineral composition too.

3.3.1 Mineralogical composition of ceramic 9 after firing at temperature 1050 ° C

Comparison of the XRD pattern of the ceramic 9 (Fig. 4) with the XRD pattern of the raw materials (Fig. 2) demonstrate the increase in the intensity of the main peaks from 1400 cps to 2100 cps, which indicates, the successful thermochemical destruction of the crystalline lattice of bauxite and its low content in the flotation sludge. On the other hand, it indicates satisfactory conditions for the synthesis of a new mineral albite ($\text{NaAlSi}_3\text{O}_8$) with more intense peak at $2\theta^\circ = 39.2^\circ$ during ceramic 9 sintering at 1050°C.

Figure 4

Almost all initial minerals of the raw materials disappeared because of thermo-chemical destruction and synthesis of other new minerals, such as magnetite Fe_3O_4 due to predominance of Fe_2O_3 (64.4%) in ferrous slag and 29.9% in red mud; paramelaconite (Cu_4O_3) due to 58.2% CuO in MSC; zincite ZnO confirmed by 24.0% in MSC; albite ($\text{NaAlSi}_3\text{O}_8$) synthesized by the presence of Al in all components; small peaks of ilmenite FeTiO_3 because of the presence of TiO_2 (2.4%) in RM.

Small decreasing of vertical scale of peaks intensity confirmed the common increase of amorphous phase in the ceramics 10 in comparison with ceramics 9. It can be one of the reasons of ceramics 10 higher flexural strength and density (Tables 3 and 5) at all temperatures before the beginning of excessive melting.

3.3.1 Morphological structure of ceramic 9 and 10 after sintering at temperature 1050° C

Better density of the morphological structure of the ceramics 10 in comparison with the ceramics 9 and after sintering at 1050°C was confirmed using SEM method (Fig. 5a and b).

Figure 5

Less quantity of open and closed pores, cracks, more completely molten particles in the structure of the ceramic sample 10 can explain these differences in the properties of the two materials. Practically all pores of the ceramics 10 are closed in a contrary of many deep (black) pores of different configurations and sizes from 1 to 18 μm of the ceramics 9. On the surface of the ceramic sample 9, unbound particles or insufficiently fused particles are clearly visible, that cannot increase the solidity and strength of the structure, in contrast to the structure of ceramics 10 with a wave of completely molten material.

3.3.2 Microchemical composition of the new formations of the ceramics 9 and 10 after sintering at temperature 1050° C

Results of EDS microchemical composition analyses of the new formations (Fig. 5) of the ceramics 9 (points 1 – 3) and 10 (points 4 – 6) after sintering at temperature 1050°C (Table 7) showed very high level of heterogeneity of all nearest points. Many parts of them were differed in the set of chemical elements and their percentage ratio neither within the limits of each ceramic, nor in comparing of these two ceramics.

Table 7 – Microchemical composition of new formations of the ceramics 9 and 10 after sintering at temperature 1050° C by EDS method (Figure 5a and b)

Points	Content of chemical elements (wt. %) in the EDS points									
	Na	Al	Si	S	Ca	Ti	Fe	Cu	Zn	Total
1	7.22	12.46	13.39	0.62	0.83	0	5.84	44.21	15.43	100.0
2	0	1.03	0	0.85	0	0	1.11	97.01	0	100.0
3	17.28	0.86	11.10	0	11.32	0	1.17	26.09	32.18	100.0
4	15.63	1.12	2.03	4.19	0	0	0.53	72.35	4.15	100.0
5	0	0	12.53	8.74	20.01	0.53	0	6.25	51.94	100.0
6	0	20.33	6.17	0	3.04	1.07	18.28	10.52	40.59	100.0
Max.	17.28	20.33	13.39	8.74	0.01	1.07	18.28	97.01	51.94	
Min.	0	0	0	0	0	0	0	6.25	0	

These results well explained the complexity of the chemical composition of the initial mixture (Table 1) for the synthesis of new minerals with a perfect crystalline structure at 1050°C, confirmed by the XRD analysis (Figure 4). Therefore, all the maximum and minimum values of all nine chemical elements of Table 7 have differences from zero to 51.94% (Zn), or from 6.25–97.01% (Cu).

3.3.3 Isotopes' composition of the ceramics 9 after sintering at temperature 1050° C

The study of the nearest points of ceramics 9 after firing it at 1050°C by the laser micro-mass analyses (LAMMA) method showed a large difference both in the composition of the isotopes and in their quantity (peak intensities). These results confirm both the results of the EDS (Fig. 5 and Table 7), and the results of the XRD (Fig. 4)

3.4 Mapping of chemical elements of the ceramic 9 after sintering at 1050°C

The method of mapping of the chemical elements on the scanning electron microscopy was used to study their distribution in a ceramic sample 9 after firing at 1050°C. This analysis made it possible to verify the great irregularity of their position for two possible reasons: 1. insufficient homogenization of the initial components before compaction and firing; 2. synthesis of microcrystals during the firing and cooling of the samples, which is confirmed by the results of the XRD (Fig. 4).

Figure 7

The maximum uniformity of distribution stands out for Ti, followed by Fe, Ca and Si the maximum unevenness had – Al, Na, Zn, Cu. But the general irregularity of the chemical element's distribution confirmed the predominant amorphism of the developed ceramic materials.

3.5 Environmental characteristics of the ceramics 9 and 10 by AAS method

3.5.1 Leaching and solubility of the developer ceramics

Leaching and solubility tests from ceramics 9 and 10 in acid solutions allows to evaluate the effect of thermo-chemical bonding of metals in the process of test samples' firing at 1050°C to prevent environmental pollution by the developed ceramics. The values of leaching and solubility is given (Table 2) in comparison with the sanitary standards [35] and initial methanol synthesis catalyst (MSC) used as the most environmentally hazardous component of the ceramics. They leaching of all hazardous chemical elements (Table 2) from ceramics 9 in comparison with MSC decreased in 13 (Se and Cr) till 110 (Cu) times: solubility – in 17 times (Cu) till 4057 times (Ba). Leaching values of the composition 10 decreased in 8 times (Cr and Se) and till 193 times (Cu); solubility values of the ceramics 10 decreased from 33 times (Cu) till 8218 times (Ba). This comparison confirmed strong chemical bonding (or mechanical capsulation) of all hazardous metals in practically insoluble new mainly amorphous glass-like formations of ceramics during their sintering at 1050°C. All obtained leaching and solubility values are significantly lower than permissible sanitary norms of Brazil [35].

3.5.2 Gas emission control results during ceramics sintering (by AAS method)

Samples of the heat gases were collected during ceramics' sintering at 1275°C in the glass filter (Figure 8) with a thickness of 0.45µm. The separation of the solid particles deposited on the filter was performed by ultrasound (three hours in an acidic medium) and determined by the AAS method (Table 8).

Table 8 - Gas emission rates during the sintering of the developed ceramic.

Heavy metals	Contents, mg/Nsm ³	[35], mg/Nm ³
Cu	1.720	5.0
Cd	0.055	0.2
Pb	0.313	5.0
Cr	0.426	5.0
Ni	0.261	1.0

Fig. 8

These results, along with leaching and solubility tests (Table 7), convincingly confirmed the robust bond of heavy metals in insoluble and non-volatile condition.

4 Conclusions

1. It was confirmed that hazardous industrial waste used in this research as the raw materials - methanol synthesis catalyst (MSC), red sludge from bauxite processing (RM) and ferrous slag (FS) – can be used as valuable raw materials for production of ceramic materials instead of traditional natural raw materials like clay and sand.
2. The best mechanical and physical properties were obtained with two ceramic compositions: 1. 40wt.% MSC, 20% RM and 40% FS, and 2. 70% MSC and 30% RM. Their flexural resistance reached 25.59 and 25.98 MPa correspondingly after sintering at 1050°C, linear shrinkage till 7.12% and 17.14%, apparent density – 3.00 and 3.46 g/cm³ and water absorption – 8.62% and 7.65%. These properties far exceeded the demands of national Brazilian demands to ceramics materials.
3. It was proved by the complex of XRD, SEM, EDS, LAMMA and chemical elements mapping methods that during the sintering of the ceramics at 1050°C the thermochemical dislocation of almost all minerals of the starting components and the synthesis of a small amount of new crystalline minerals occurred. However, the decisive role in the formation of the structure and properties of the developed ceramics is played by amorphous glassy formations, which filled pores of the materials.
4. By the method of atomic absorption analysis of a liquid extract obtained in an acidic medium, it has been established that the developed ceramic materials firmly bind or reliably encapsulate all hazardous elements into an insoluble state. This allows to use them as building materials, and at the end of their service, their demolition waste can be used as crushed stone for the production of new environmentally friendly building materials. This allows the use of a large amount of hazardous industrial waste as a valuable raw material, improving the environment of the industrial region. At the same time, it becomes

possible to sharply reduce the destruction of unrecoverable natural ties by quarries of natural building materials.

5. The calculation of the economic efficiency of the production of developed materials was not part of the purpose of this study, because each time it depends on many specific local parameters. But from the common sense, the use of free raw materials (hazardous industrial waste) instead of costly natural building material is always much more profitable.

Declarations

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Conflicts of interest and others Declarations

- a. Funding (information that explains whether and by whom the research was supported)
- b. We declare absence any conflicts of interest
- c. Data and material are available
- d. Code availability (software application or custom code) not applicable
- e. Ethics approval (include appropriate approvals or waivers) not applicable
- f. We show informed consent and provide assurances that participants' rights are protected
- g. All co-authors are consent for publication
- h. Authors' contributions

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Figures

a

b

Figure 1

Appearance of the waste of methanol synthesis catalyst:

a - original; **b** - dry and milled.

Figure 2

Diffractogram patterns of the raw materials:

a – Waste of methanol synthesis catalyst, **b**– Red mud, **c** – Ferrous slag.

Figure 3

Morphological microstructures of the raw materials:

a – Waste of methanol synthesis catalyst, **b** – Red mud, **c** – Ferrous slag.

Figure 4

XRD patterns of the ceramics 9 (**a**) and 10 (**b**) after sintering at 1050°C

Figure 5

Morphological structure of the composites 9 (a)
and 10 (b) sintered at 1050°C and points of EDS analyses

Figure 6

Isotopes' composition of the nearest points of the ceramics 9.

Figure 7

Mapping of chemical elements of the ceramic 9 after sintering at 1050°C

Figure 8

Electric oven with gas filter.