MATERIAIS A BASE DE RESÍDUOS DE PORCELANA INDUSTRIAIS PARA UTILIZAÇÃO EM CONSTRUÇÕES AMBIENTALMENTE AMIGÁVEIS

ENVIRONMENT FRIENDLY CONSTRUCTION MATERIALS ON THE BASE OF PORCELAIN INDUSTRY WASTES

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Resumo

Um novo método foi desenvolvido e patentado para o uso de três tipos de resíduos para manufatura de telhas de porcelana – resíduos queimados (RQ), resíduos não queimados (UW) e residos de tratamento de agua (RTA) – como a matéria prima principal para produção de novos materiais de construção. O material ligante utilizado foi o resíduo da produção de cal (RPC). A resistência axial dos novos materiais que continham 15% de RPC e um ano cura aumentou até 14.2 MPa e os materiais com o conteúdo de RPC de 5% aumentaram até 8.6 MPa, excedendo as especificações dos padrões brasileiros de blocos de concreto. O coeficiente de absorção de água (CA) de diferentes composições com 28 dias de cura variou de 17.9 a 24.6%, mas isto não afetou os valores do coeficiente de resistência à água (0,71 a 0,85). A difração de raios X e a análise por microscopia eletrônica indicaram que a resistencia dos novos materiais aumentou devido à síntese de compostos amorfos e cristalinos. A viabilidade de uso destes novos materiais é baseada na utilização de quatro tipos de resíduos industriais para a produção de novos materiais para a construção civil por apresentarem boas propriedades mecânicas e que satisfazem as condições nacionais dos padrões de saúde.

Palavras-chave: Resíduos da indústria de porcelana. Resíduos da produção de cal. Novos materiais. Construção civil. Processos físico-químicos.

Abstract

A new method was developed and patented for the use of three types of wastes from the manufacture of porcelain tiles – fired wastes (FW), unfired wastes (UW) and wastewater treatment plant sludge (WTPS) – as the main raw materials for the production of new construction materials. The binder material used here was lime production waste (LPW), i.e., incompletely burned lime. The un-axial compressive strength of the new materials containing 15 wt% of LPW at one year of age increased up to 14.2 MPa and the materials with 5% LPW content increased up to 8.6 MPa, exceeding the specifications of Brazilian standards for hollow concrete blocks. The water absorption (W_A) coefficient of different compositions at the age of 28 days ranged from 17.9 to 24.6%, but this does not affect the values of the water resistance coefficient (0.71 to 0.85). X-ray diffraction and scanning electron microscopy analyses indicated that the strength of the new materials increases due to the synthesis of amorphous and crystalline compounds. The feasibility of the new materials is based on the use of four types of industrial wastes for the production of new construction materials with high mechanical properties, which meet the requirements of national health standards.

Keywords: Porcelain industry wastes. Lime production wastes. New materials. Civil construction. Physicochemical processes.

1 Introduction

The strategy of companies to improve their environmental performance is an essential part of their social function, since it not only satisfies their clients' wishes, but also improves their relationships with environmental control agencies and with society in general. Mere compliance with the minimum standards established by environmental laws is not considered sufficient to maintain a competitive advantage, above all in export markets (HAWKEN; LOVINS; LOVINS, 1999).

The solid wastes from the manufacture of ceramic tiles are produced during the pressing and milling steps, the so-called "Unfired Wastes" (UW), whose reuse is insufficient to eliminate this environmental liability from the manufacturing process. However, today, the main problem in this segment is the wastes generated after the firing step, called "Fired Wastes" (FW). These wastes consist of finished ceramic products that present disqualifying faults. The volume of this discarded material represents, on average, 3.0% of the entire domestic production of ceramic tiles. Equating this figure with the actual production volume indicates a major environmental problem. Moreover, dumping this material in specific areas (landfills) is a palliative measure which is also harmful. On the other hand, the problem in reusing FW stems from the fact that this material is very hard, which makes it difficult to introduce it directly into the process since doing so would significantly increase the costs of processing the material (FERRARI; FERRI; SILVA, 2002; SÁNCHEZ-ROJA *et al*, 2003).

In the preparation of ceramic bodies, glazes and glazing lines, ceramic tile manufacturing generates considerable emissions, effluents and wastes that require investments in various types of

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equipment for treatment and/or proper disposal. These wastes are generated by cleaning equipment, by production wastes, and in the case of ceramic slip wastes, by sieving the slip before atomizing it. The effluents are treated in wastewater treatment plants, resulting in sludge, which is dewatered in a filter press and compacted into blocks commonly called sludge cake or simply WTPS (LORENZI, 2005; NANDI *et al.,* 2010)

The most important aspect in making use of the results obtained in studies about the reuse of lime production wastes (LPW) may be the environment aspect, in view of the real possibility of significantly reducing currently existing deposits of lime wastes, whose pH levels are extremely high. With the exception of large companies that use modern techniques, most lime is produced in a highly impactful way that involves digging large pits and generating emissions of gases and particulate pollutants during the fabrication of these derivatives (KUMAR; SINGH, 1998; MYMRIN; CORREA, 2007).

LPW is poorly calcined and noncompliant with the specifications of Brazilian standards, characterizing it as being of low reactivity. LPW is composed primarily of non-hydrated calcium oxide, calcium hydroxide, rests of unburned calcium carbonate and magnesium, and non-hydrated magnesium oxide (GUIMARÃES; GOMES; SEABRA, 2004).

2 Objectives of this work

a) Help porcelain manufacturers to minimize their environmental impacts.
b) Develop new materials for civil construction with maximum content of industrial wastes to conserve natural raw materials.
c) Develop new materials that are environmentally friendly, economically viable, and whose properties are better than those established by Brazilian standards.
d) Study the physicochemical processes involved in the formation of the structures of new materials, aiming to obtain materials with predetermined mechanical properties.
e) Develop new technologies or adapt current ones for the production of new materials.

3 Results and discussion

3.1 Raw materials and research methodology

The following sequence was adopted to obtain the experimental results: collection, preparation and characterization of the wastes, definition of the compositions of the mixtures, manufacturing and testing (mechanical and physicochemical) of the test specimens.

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A ceramic tile manufacturer located in the region of Campo Largo, state of Paraná, Brazil supplied three types of wastes: fired wastes (FW), unfired wastes (UW) and wastewater treatment plant sludge (WTPS).

A quicklime plant located in the region of Colombo, state of Paraná, Brazil supplied LPW – the incompletely burned lime, which was used in these experiments as binder in the mixtures.

Lime used as a binder in construction material must present a minimum total nonvolatile oxide content of 88% (CaO + MgO) and a maximum carbon dioxide (CO_2) content of 12%, according to the Brazilian standard NBR 6453/2003. As can be seen in Table 1, the LPW used in this study presented contents of 23.9% CO_2, 45.1% CaO and 28.3% MgO, thus characterizing it as lime production waste.

The chemical composition of the raw materials (Table 1) determined by X-ray fluorescence spectroscopy (XRF) shows that the main content (up 84.7%) of elements in the wastes (FW, UW and WTPS) supplied by the porcelain manufacturer represents SiO_2 and Al_2O_3. The dolomite LPW has the same majority of CaO and MgO – up to 73.4 wt% plus 23.9 wt% of CO_2 in the form of carbonates.

Table 1 – Chemical composition of the raw materials determined by XRF

Oxides	Compositions, wt.%			
	FW	UW	WTPS	LPW
SiO_2	64.1	65.9	63.0	1.9
Al_2O_3	20.6	18.1	23.4	0.2
CaO	7.8	7.3	7.7	45.1
MgO	2.0	1.3	0.9	28.3
K_2O	1.7	2.0	1.8	0.2
Fe_2O_3	1.5	0.8	1.3	0.4
TiO_2	1.0	0.5	1.0	-
Na_2O	0.8	1.3	0.5	-
ZrO_2	0.2	1.2	0.1	-
ZnO	0.1	1.2	0.1	-
BaO	0.1	0.3	0.1	-
P_2O_5	0.1	0.3	0.1	-
CO_2	-	-	-	23.9
PF	1.4	7.4	11.4	27.9

Figure 1 shows the particle size distribution curves of the raw materials. The LPW, FW, WTPS and UW present an average particle size of 70, 100, 260 and 750 μm, respectively, with 100% of the distribution smaller than 0.80 mm.

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Figure 1 – Particle size distribution curves of the raw materials determined by method of Laser granulometry. Where: Fired waste (FW); Unfired wastes (UW); Wastewater treatment plant sludge (WTPS); Lime production waste (LPW)
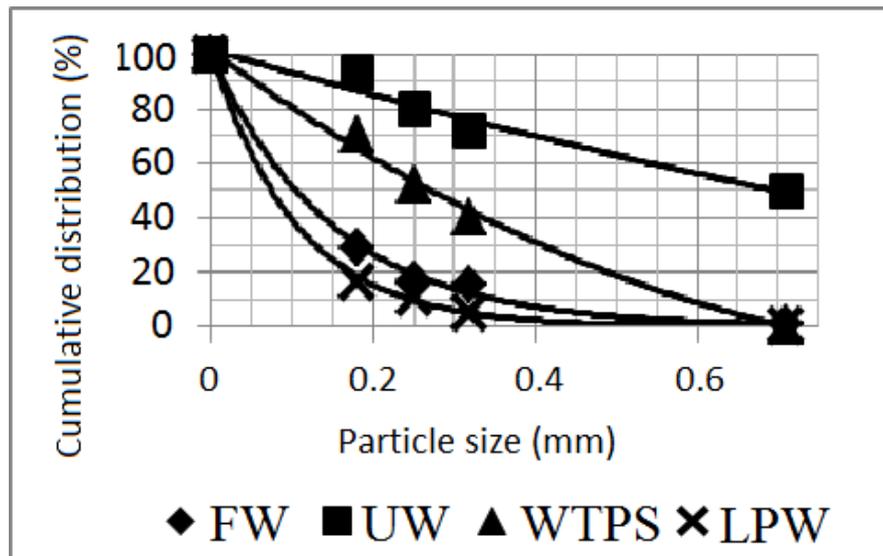
The mineralogical composition (Table 2) determined by X-ray diffraction (XRD) demonstrates the high complexity of the components of the raw materials.

Table 2 – Mineralogical composition of the raw materials determined by XRD

Components	Minerals		Components	Minerals	
Fired Wastes (FW)	Quartz	SiO_2	Wastes treatment plants sludge (WTPC)	Quartz	SiO_2
	Labradorit	$(Na_{0.4}Ca_{0.6})Al_{1.6}Si_{2.4}O_8$		Labradorit	$(Na_{0.4}Ca_{0.6})Al_{1.6}Si_{2.4}O_8$
	Calcite	$CaCO_3$		Calcite	$CaCO_3$
	Mullit	$Al(Al_{0.69}Si_{1.22}O_{4.85})$		Dolomit	$CaMg(CO_3)_2$
	Dolomite	$CaMg(CO_3)_2$		Zircon	$Zr(SiO_4)$
Unfired Wastes (UF)	Quartz	SiO_2		Kaolinite	$Al_2Si_2O_5(OH)_4$
	Calcite	$CaCO_3$		Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$
	Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$	Lime production waste (LPW)	Cal	CaO
	Cristobalit	SiO_2		Portlandit	$Ca(OH)_2$
	Dolomite	$CaMg(CO_3)_2$		Periclase	MgO
	Kaolinit	$Al_2Si_2O_5(OH)_4$		Calcite	$CaCO_3$
	Zircon	$Zr(SiO_4)$		Quartz	SiO_2

To achieve the objectives of this research, the mixtures were homogenized, hydrated, compacted in a cylindrical mold into dimensions of 20 x 20 mm under a pressure of 10 MPa, and cured in the open air for 1, 3, 7, 17, 28, 60, 90 , and 180 days, and one year.

3.2 Mechanical properties of the new materials

According to Figure 2, all the compositions exhibited increased strength with increasing binder (LPW) content and curing time. Therefore, the highest strengths at the age of one year were achieved by compositions A and D, with LPW content of 15 wt% (14.21 and 13.96 MPa, respectively), and the lowest by compositions C and F, with LPW content of 5 wt% (8.56 and 6.16 MPa, respectively). When 30 wt% of WTPS was used, the un-axial compressive strength of the new materials decreased, although its properties were not significantly affected. Therefore, a

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solution for the environmental burden represented by WTPS is its incorporation into the final product, without significantly reducing its properties.

Figure 2 – Summary of the results of un-axial compressive strength of the developed materials.
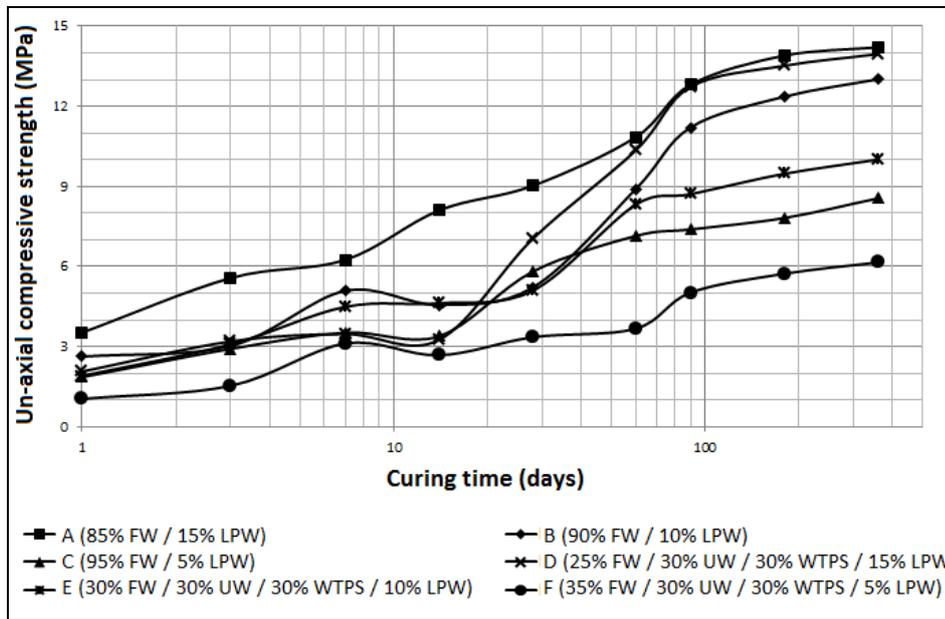
In the manufacture of plain hollow concrete blocks for class D non-structural masonry, the Brazilian standard NBR 12118/2010 requires a un-axial compressive strength of 2.0 MPa after 28 days of curing time. A comparison of the values shown in Figure 2 indicates that all the compositions at 28 days of age exceeded the un-axial compressive strength required by the standard.

The standard deviation of all the materials also varied from 0.11 to 1.09 MPa according to their curing time and composition.

The coefficient of water resistance (Cw) was determined based on the ratio:

$$C_W = R_{SAT}/R_D \qquad (1)$$

Where

R_{SAT} - the un-axial compressive strength of test specimens saturated after total immersion in water for 24 hours,

R_D - the un-axial compressive strength of the specimens oven-dried at 100°C for 24 hours.

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Table 3 – Coefficients of water resistance (C_W) and of water absorption (C_A) on the 28-th day

Compositions	Un-axial resistance strength (MPa)		Water resistance coefficient (Cw)	Water absorption coefficient (C_A) wt.%
	"Dry" (R_D)	Saturated (R_{SAT})		
A	12.81	10.90	0.85	24.62
B	11.21	8.49	0.76	24.81
C	7.39	5.26	0.71	23.78
D	12.73	10.55	0.83	18.52
E	8.71	6.48	0.74	17.74
F	5.03	3.61	0.72	17.92

Water absorption (W_A) tests were performed with specimens cured for 28 days (Table 3), in accordance with the Brazilian standard NBR 9778/2009, which uses the following equation:

$$W_A = [(M_{SAT} - M_D)/M_D] \times 100 \tag{2}$$

Where

M_{SAT} is the mass of the saturated specimen after 24 hours of immersion in water and

M_D is the mass of the specimen oven-dried at 100°C for 24 hours.

The increase in water absorption of over 17% between the compositions of the mixtures (Table 3) did not significantly reduce the un-axial compressive strength of the materials. This behavior is directly related to the presence of the binder (LPW). The average water absorption of ordinary hollow concrete masonry blocks with lightweight aggregate is at the most 13%, according to the standard NBR 12118/2010.

Shrinkage increased almost linearly from 0.28% – 1.27% on day 3 up to 1.43% – 1.92 % in 180 days, in response to increasing LPW content.

3.3 Physicochemical processes of structure formation

The interpretation of X-ray diffraction patterns of samples with large quantities of mineral components is not completely accurate due to overlapping of some of the peaks of different minerals. However, despite this difficulty and possible inaccuracies, the changes in the peak intensities of the greatest transformations can be attributed to the hydration of the compositions and strengthening of the test specimens.

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Figure 3 – Change of X-rays diffractogram of the composition A during the hydration: A – 28 days, B – 90 days and C – 180 days.

| A | B | C |
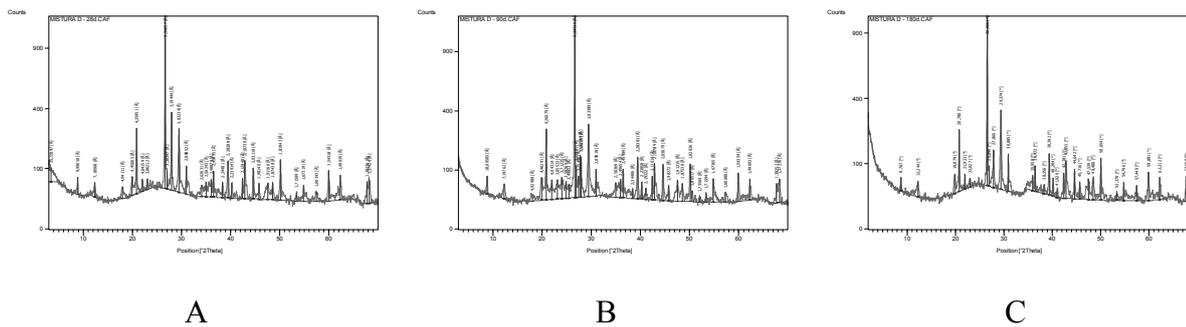
The two main processes that take place in materials during their hydration and curing time are the dissolution of some of the minerals of raw materials and the synthesis of new minerals. The dissolution was characterized by the decrease in peak intensities or the complete disappearance of some minerals, while synthesis was characterized by the emergence of new crystalline peaks.

A comparison of the X-ray diffractions of mixture A (Figure 3) in the initial phase (dry) on day 28, 90 and 180 revealed the following changes in the minerals: Dolomite $[CaMg(CO_3)_2]$, Mullite $[Al(Al_{0.69}Si_{1.22}O_{4.85})]$ and Portlandite $[Ca(OH)_2]$ – peaks were observed only in the initial mixture (dry). Calcite $[CaCO_3]$ – the peaks increased in intensity throughout the study. Quartz $[SiO_2]$ and Cristobalite $[SiO_2]$ – the intensities of the peaks changed only slightly throughout the study. Gelenite $[Ca_2Al_2SiO_7]$ – peaks appeared on day 28 and increased in intensity throughout the study. Labradorite $[(Na_{0.4}Ca_{0.6})Al_{1.6}Si_{2.4}O_8]$ – the intensity of the peaks decreased at the onset of hydration and disappeared completely by day 90. Lime $[CaO]$ and Periclase $[MgO]$ – the intensity of the peaks decreased at the onset of hydration and disappeared completely by day 180.

The minor variation in the increased intensity of the peaks corresponding to Calcite and Gehlenite cannot explain the increase in un-axial compression strength above 14 MPa. One of the authors [6] of this paper exhaustively researched other materials with similar behavior, using LPW as binder. He found that a significant amount of amorphous new formations were synthesized, which can also strengthen these materials. These formations may include amorphous carbonates, particularly in the early stages of hydration, which is also consistent with the XRD results described above.

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Figure 4 – SEM micrographs on day 180 of curing under 2,000 X magnification of: (a) mixture A, and (b) mixture D

a x 2,000 |———— 50µm ————| b x 2,000 |———— 50µm ————|
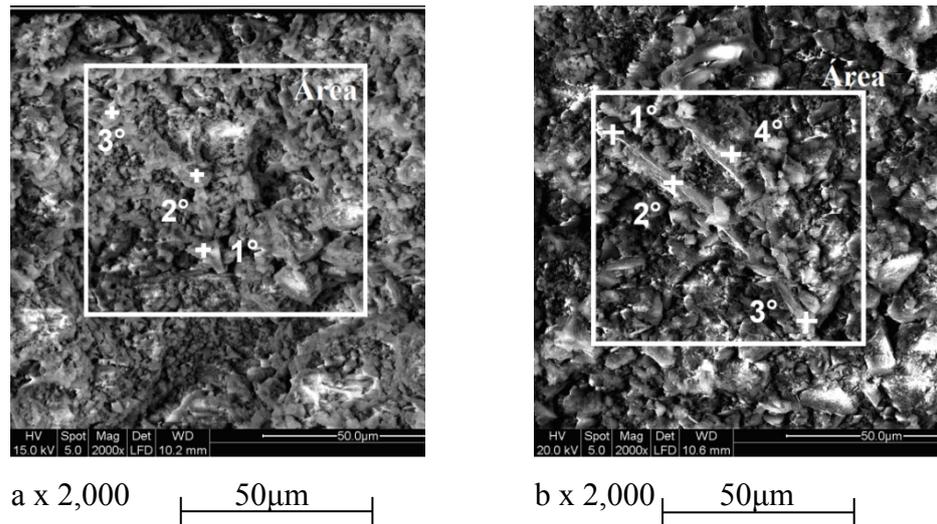
Table 4 – Chemical composition determined by EDS of the sample A (Figure 4-a) on the 180-th day of hydration

Spectrum	C	Na	Mg	Al	Si	K	Ca	Ti	Fe
Area	17.20	-	5.68	9.73	19.77	2.60	41.66	0.42	1.35
Point 1	25.95	-	4.56	10.08	26.58	3.07	26.04	1.23	2.50
Point 2	29.12	-	2.74	11.40	33.95	2.25	18.80	0.48	1.27
Point 3	27.89	0.81	2.14	18.20	31.80	6.21	8.87	0.99	3.09

Table 5 - Chemical composition determined by EDS of the sample D (Figure 4-a) on the 180-th day of hydration

Spectrum	C	Na	Mg	Al	Si	K	Ca	Ti	Fe
Area	24.14	0.83	2.22	11.67	34.28	12.11	12.10	0.44	2.20
Point 1	33.21	0.82	3.53	10.34	28.36	3.74	16.30	1.01	1.30
Point 2	23.19	0.40	2.95	9.43	22.76	18.78	18.10	0.85	3.54
Point 3	28.01	0.57	3.76	12.36	24.91	4.13	21.28	1.21	3.78
Point 4	24.17	-	3.11	12.83	28.33	6.89	18.69	0.99	3.00

The appearance of these amorphous materials is more clearly visible when analyzing the materials by scanning electron microscopy (SEM). The micrograph of the initial mixture of the dry components (Figure 3-A) under 2,000X magnification shows heterogeneous free-standing particles of different sizes, which do not interact chemically, and with large quantities of inter-particle pores. The areas inside the circles in the micrographs of mixtures A and D cured for 180 days (Figure 3-B and C), magnified 2,000X times, show more structured and bonded materials, albeit without a defined structure. The images of new formations reveal an absence of crystal structures, but show similar formations of amorphous structures. If crystals are not responsible for this considerable increase in un-axial compressive strength, the only plausible explanation is the growth of new amorphous formations.

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Figure 5 – EDS specters of the areas, FIGURA 4-a,b of the mixture A and D on the 180-th day of curing

a   b
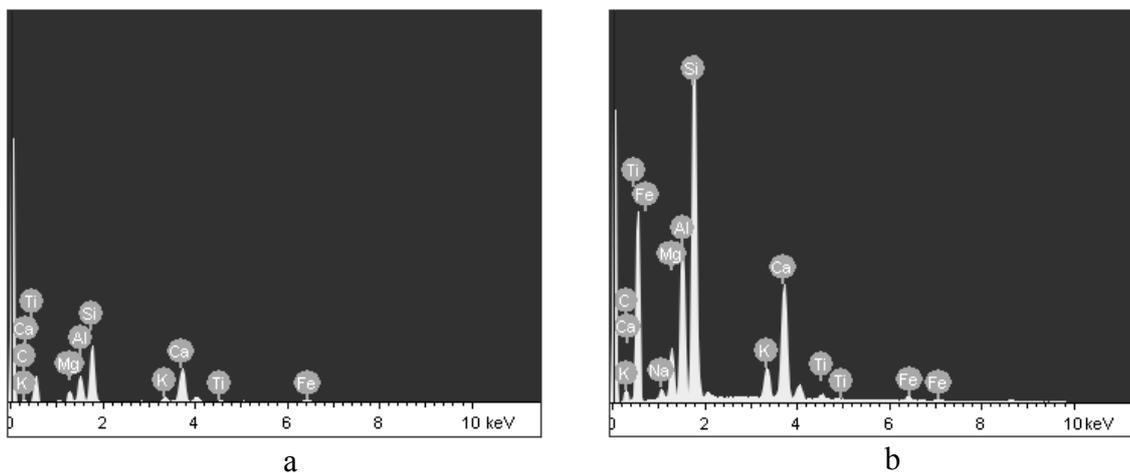
The chemical compositions of areas revealed by EDS images (Figure 5) and the points indicated in Figure 4 are described in Tables 4 and 5. The chemical compositions of the areas are in agreement with the XRF results (Table 1) and the compositions at points in Table 4 and 5 confirm the XRD results (Table 2 and Figure 3). New formations at two compared areas are very different, as well as of the points 1- 3 of Table 4, especially of value of Si, K and Ca. The compositions of points 1 – 4 on the surface of the largest lengthened particle of Figure 4-b are rather similar. But significant variations in the content of some elements, especially of K (from 3.74 till 18.78%), do not permit to attribute them to the crystalline form, confirming the presence of amorphous structures of new formations, responsible for all materials mechanical properties (un-axial resistance strength, water resistance, water absorption, shrinkage, etc.).

4 Conclusions

1. The porcelain tile wastes studied here can be used as the main raw material for new construction materials with mechanical properties similar to those of concrete, provided lime production waste (LPW) is used as binder.

2. The mechanical properties of the materials developed in this work exceed the requirements of the Brazilian technical standards. The un-axial compressive strength increases with increasing binder content (LPW) and curing time. This strength increased to 5.57 MPa on day 3, to 9.03 MPa on day 28, to 13.90 MPa on day 180, and to 14.21 MPa on day 360. The high of water absorption rate at the age of 90 days (17.92 to 24.62%) did not affect the coefficient of water resistance (C_w), which varied in the compositions from 0.71 to 0.85; shrinkage increased almost linearly up to 1.92 % in 180 days. The high mass fractions of WTPS (30%) hardly affected the mechanical properties of the new materials.

3. Based on XRD and SEM analyses, it was found that, during the hydration and curing time of the mixtures, three main groups of minerals with different behaviors occurred, as follows. Partial or

complete dissolution of the minerals of the initial mixtures – Mullite [Al(Al$_{0.69}$Si$_{1.22}$O$_{4.85}$)], Labradorite [(Na$_{0.4}$Ca$_{0.6}$)Al$_{1.6}$Si$_{2.4}$O$_8$], Portlandite [Ca(OH)$_2$], Lime [CaO] and Periclase [MgO]; Synthesis of new minerals – (Gehlenite [Ca$_2$Al$_2$SiO$_7$]), and significant amounts of new amorphous materials, especially carbonates, or increased amounts of Calcite [CaCO$_3$]; and neutral, i.e., minerals whose peak intensities remained practically unchanged – Quartz [SiO$_2$] and Cristobalite [SiO$_2$].

4. The scope of this research did not include calculations of economic efficiency, but common sense suggests that the use of industrial wastes in place of natural raw materials, in view of the low cost of these wastes compared to that of traditional materials, must be very lucrative.

5. The most important benefit obtained by using the findings of this study is environmental, in view of the real possibility of using various industrial wastes as raw materials, as a suitable form of disposal, thereby preventing potential environmental contamination and minimizing the extraction of natural resources.

Acknowledgements

References

FERRARI, K. R.; FERRI, C. R.; SILVA, L. L. Ações para a diminuição da geração de resíduos na indústria de revestimentos cerâmicos. **Cerâmica Industrial**, v. 7, n. 2, p. 38-41, 2002.

GUIMARÃES, J. E. P.; GOMES, R. D.; SEABRA, M. A. **Guia das argamassas nas construções: construindo para sempre com cal hidratada**. 8. ed. São Paulo: Brazilian Association of Lime Producer, 2004.

HAWKEN, P.; LOVINS, A.; LOVINS, L. H. **Capitalismo natural**: criando a próxima revolução industrial. São Paulo: Cultrix, 1999. 358 p.

KUMAR S.; SINGH L. P. Utilization of FaL-G bricks in low cost housing. In: National Seminar on Environmental Aspects of Engineering Practices, 1998, Jhansi, India. **Proceedings..**. Jhansi: B.I.E.T, 1998.

LORENZI, V. **Reaproveitamento do resíduo sólido proveniente da estação de tratamento de efluentes da indústria cerâmica de grês porcelanato**. 2005. 120 f. Dissertação (Mestrado em Ciências Ambientais) – Universidade do Extremo Sul Catarinense, Criciúma, 2005.

MYMRIN V.A.; CORREA S. M. New construction material from concrete production and demolition wastes and lime production waste. **Construction and Building Materials**, v. 21, n. 3, p. 578-582, 2007.

NANDI, V. S. et al. Reaproveitamento de Lodo Cerâmico de Estação de Tratamento de Efluentes para a Produção de Esmaltes. Cerâmica Industrial, v. 15, n. 1, p. 34-37, 2010.

SÁNCHEZ-ROJA, M. I.; FRI´AS, M., RIVERA, J.; MARI´N, F. P. Wastes products from prefabricated ceramic materials as pozzolanic addition. In: International Congress on the Chemistry of Cement (ICCC): Cement's Contribution to Development in the 21st Century, 11th ed., 2003, Durban. **Proceedings…** Durban: Cement Concrete Institute of South Africa, 2003. p. 935–43.

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