NATURAL DIOPSIDE: A NEW RAW MATERIAL FOR PORCELAIN TILES

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1. ABSTRACT

In the central NW of Bahia state, Brazil, along the Paleoproterozoic "Itabuna-Salvador-Curaçá" orogenic belt, diopside-rich calcium silicate rocks containing several lenses of massive white diopsidite occur. At least two mines are found in this region. The material is supplied to ceramic tile industry for engobe use. Chemical composition for the standard material is (in wt%): SiO_2- 55,0; Al_2O_3- 3,0; Fe_2O_3- 0,6; MgO- 17,5; CaO- 20,5; Na_2O- 0,5; K_2O- 1,0; and L.O.I -0,5.

Geological and mineralogical studies have pointed out four main units containing diopside: I) massive diopsidite, containing more than 70% of diopside and small amounts of carbonate, feldspars, quartz, tremolite and phlogopite; II) quartz diopsidite, containing scapolite, garnet, titanite, plagioclase and wollastonite; III) microcline/orthoclase diopsidite, which may contain quartz; and VI) calcium-silicate gneisses with intercalations of quartz-feldspathic bands and diopside-rich bands. The lithotypes have white, grey or light green to dark green staining, and fine to very thick

granulation. Important lenses of massive diopsidite (unit I) have already been evaluated, including details of mineralogy and chemical composition. These rocks show the following mineral composition: diopside (70-95%), quartz (5-30%), K-feldspar (5-15%).

Experiments indicate good performance when diopsidite is added in the composition of technical and glazed porcelain tile bodies, engobe and glazes. Diopside improves the whiteness, allows sintering at lower temperatures, promotes reduction in the flow time of the suspensions and higher concentration of solids of the slurry and increases opacity of glazes.

Mineral research to measure resources and reserves of diopside are still ongoing, but good reserves have already been found. Further studies involving the chemical, mineralogical and technological characterization of diopside, in order to develop new applications of this material in ceramic and other industries, are still ongoing as well.

2. INTRODUCTION

Either by necessity or due to technical-economic advantages, the Brazilian ceramic industry is searching for alternative industrial ceramic minerals to replace the traditional raw materials of triaxial porcelain —quartz, feldspar and kaolin.

Among these substitute minerals, phyllite stands out, initially used in sanitary ware and later in the ceramic tiles industry, as well as other minerals such as granite, phonolite, nepheline, philonite, etc.

In an extreme case, the Brazilian industry replaced the entire blend of the ceramic body with a single clay to produce semi-porous ceramic tiles. In this case, additionally, the industry developed a particular dry route to simplify and cheapen the milling process.

Currently, with increasing production of porcelain tiles coupled with the increase in the size of pieces, there is higher demand for feldspar and other minerals which contribute to improved performance in the production process and the final products.

Diopside is being studied in this context, since this material is available in large quantities and qualities and, according to several authors [1-4], may contribute to the targeted performance.

The studies involved field surveys, with mapping of diopside lenses and sampling, and mineralogical, chemical and physical characterization. Part of the geological characterization has been presented before [5]. In addition, studies were carried out for application in ceramic bodies of porcelain stoneware, engobes and glazes. These are presented and discussed here..

3. GEOLOGICAL, MINERALOGICAL AND CHEMICAL CHARACTERISTICS

In Brazil, since 2010, new deposits of diopside, a mineral which application is restricted to the composition of engobes, have been studied and exploited in Bahia. These occurrences are being studied regarding their geological, mineralogical and chemical characteristics and some results have already been presented [5].

Geologically, the region studied is part of the Archean-Paleoproterozoic orogenic belt. It is formed of high grade metamorphic rocks (orthogneisses and migmatites), containing strips of calc-silicate rocks with discontinuous layers or lenses of white and massive diopsidite, composed of diopside (70-95%), quartz (0-20%), feldspar (0-15%), and other minor minerals such as carbonates, phyllosilicates, garnet, scapolite, sphene and wollastonite.

The average composition of the standard commercial type is: SiO_2 - 55%; Al_2O_3- 3%; Fe_2O_3- 0.6%; MgO- 17.5%; CaO- 20.5%; Na_2O- 0.5%; K_2O- 1%; and L.O.I- 0.5%.

Figs. 1 and 2 show diopside crystals observed under polarized microscopy.

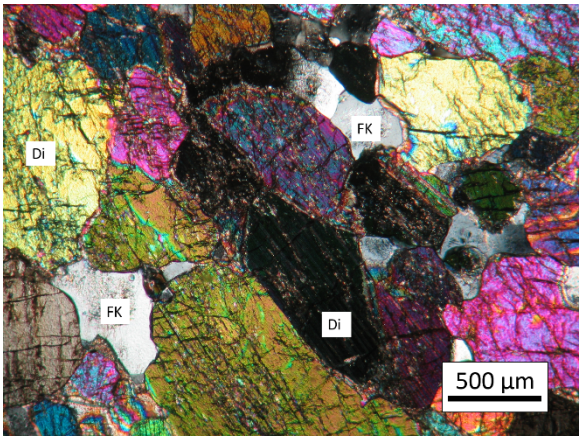

Fig. 1 *Diopsidite formed of diopside (Di and most of crystals) and feldspar (fk) and quartz.*

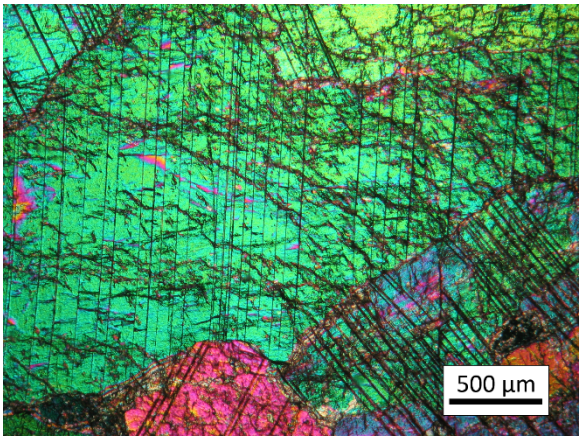

Fig.2 *Larger crystals of diopside*

4. EXPERIMENTAL

For the LAB tests the above-mentioned standard diopside was used. The objectives of these studies were to evaluate:

(a) the incorporation of diopside into ceramic bodies of technical porcelain tile, aiming at the total or partial replacement of zircon used in a reference ceramic body composition;

(b) the technical feasibility of incorporating diopside into a ceramic body of glazed porcelain tile;

(c) the technical feasibility of incorporating diopside into refractory and impermeable engobe compositions; and

(d) the technical feasibility of incorporating diopside into matte glaze compositions for use in ceramic tiles.

(a) Experimental studies for technical porcelain tile

The raw material was incorporated into a typical composition of technical porcelain tile, with total and partial replacement of the zircon used in the standard composition (PT-STD). For this, four porcelain tile compositions were prepared, as indicated in Table 1.

The raw materials were dosed according to the compositions set out in Table 1 and milled in a ball mill with the incorporation of water (50%) and sodium silicate (0.7%). The grinding was carried out in order to reach residue in ABNT #325 (45 µm) sieve below 2.0%. After discharging the mills, the density and viscosity of the suspensions were comparatively characterized

Raw Material (%)	Composition of ceramic bodies			
	PT – STD	PT – 01	PT – 02	PT – 03
Kaolin	25.0	25.0	25.0	25.0
Talc	4.0	4.0	2.0	-
Albite	32.0	32.0	32.0	32.0
K Feldspar	20.0	20.0	20.0	20.0
Clay 1	8.0	8.0	8.0	8.0
Clay 2	4.0	4.0	4.0	4.0
Bentonite	4.0	4.0	4.0	4.0
Zircon	3.0	-	-	1.5
Diopside	-	3.0	5.0	5.5

Table 1. *Technical porcelain tile body composition*

The ground material was dried in an electric oven, disaggregated in a mortar and granulated with 6.5% water. Next, prismatic specimens of 60 x 20 x 6 mm^3 were pressed in a laboratory hydraulic press with application of 450 kgf/cm^2 of compression pressure. The specimens obtained were dried in an electric oven at 110 °C and characterized with respect to their apparent density.

Then, the bodies were fired at four different temperatures, in firing cycles of approximately 60 minutes. These samples were characterized regarding their water absorption (AA) and linear retraction for the evaluation of the vitrification curves. The apparent porosity and density of the fired pieces were also evaluated by the Archimedes method. The specimens at the temperature at which they reached water absorption ≤ 0.1% (normative specification for technical porcelain tiles) were evaluated with respect to their flexural modulus (MRF) by the 3-point flexural test, colour of burning (through the colour coordinates measured in a spectrophotometer) and pyroplasticity index

(b) Experimental studies for glazed porcelain tile

The raw material was incorporated into a typical glazed porcelain tile composition used locally in Brazil in proportions of 2, 5 and 10%. For this, four compositions were prepared, as indicated in Table 2, where the PE-STD is the standard formulation, without addition of diopside.

Raw Material (%)	Composition of ceramic bodies			
	PE – STD	PE – 02	PE – 05	PE – 10
Clay 1	15.0	14.7	14.3	13.5
Clay 2	18.0	17.6	17.1	16.2
Clay 3	7.0	6.9	6.6	6.3
Feldspar	10.0	9.8	9.5	9.0
"Filito" (phyllite)	44.0	43.1	41.8	39.6
Talc	6.0	5.9	5.7	5.4
Diopside	-	2.0	5.0	10.0

Table 2. *Glazed porcelain tiles composition*

The raw materials were dosed according to the compositions set out in Table 2 and milled in a ball mill with the incorporation of water (53%) and sodium silicate (0.8%). The grinding was carried out in order to reach residue in ABNT #230 (63 μm) sieve between 5 and 10%. After discharging the mills, the density and viscosity of the suspensions were comparatively characterized.

The ground material was dried in an electric oven, disaggregated in mortar and granulated with 7.0% water. Next, prismatic specimens of 60 x 20 x 6 mm^3 were pressed in a laboratory hydraulic press with application of 380 kgf/cm^2 of compression pressure. The test specimens were dried in an electric oven at 110 °C and characterized in terms of apparent density, flexural modulus (MRF), their flexural modulus (MRF) by the 3-point flexural test and linear drying retraction.

Next, the bodies were fired at four different temperatures, in firing cycles of approximately 45 minutes. These samples were characterized regarding their water absorption (AA) and linear retraction for the evaluation of the vitrification curves. The apparent porosity and density of the fired pieces were also evaluated by the Archimedes method. The specimens fired at the temperature at which they reached water absorption ≤ 0.5% (normative specification for glazed porcelain tiles) were evaluated with respect to their flexural modulus, colour of burning (through the colour coordinates measured in a spectrophotometer), pyroplasticity index and thermal expansion coefficient.

(c) Experimental studies for engobes

Two typical engobe compositions have been formulated, an impermeable one and a refractory one.

In the case of the impermeable engobe, diopside was incorporated into the composition by partially and totally replacing the zircon, as indicated in Table 3.

In the formulations of refractory engobes, diopside was added in amounts of 10% and 20%, maintaining the proportion of the other raw materials used in the composition as indicated in Table 4.

Raw material (%)	Composition of engobes		
	EI – STD	EI – 04	EI – 08
Quartz	15.0	15.0	15.0
Clay "Queijo"	14.0	14.0	14.0
Frit 1292 FR006	20.0	20.0	20.0
Frit FTB003 FR007	15.0	15.0	15.0
Feldspar	20.0	20.0	20.0
Zircon	8.0	4.0	0.0
Bentonite	1.0	1.0	1.0
Talc	5.0	5.0	5.0
Kaolin CR	2.0	2.0	2.0
Diopside	-	4.0	8.0

Table 3. *Composition of impermeable engobes*

Raw material (%)	Composition of engobes		
	ER – STD	ER – 10	ER – 20
Quartz	28	25.2	22.4
Clay	18	16.2	14.4
Frit FR006	8	7.2	6.4
Feldspar	18	16.2	14.4
Bentonite	0.5	0.5	0.4
Talc	4.5	4.1	3.6
Kaolin	5	4.5	4
Diopside	-	10	20
Glass	18	16.2	14.4

Table 4. *Composition of refractory engobes*

The compositions were milled in a laboratory mill with water equivalent to 40% of the total mass of the raw materials and 0.4% of sodium tripolyphosphate. The densities of the suspensions obtained were determined in a pycnometer, whereas the apparent viscosities were determined in a Brookfield rotational viscometer at 30 RPM and estimated in the Ford cup No. 4. The residue content of the engobes was also determined by wet sieving in ABNT #325 sieve (45 μm aperture). The engobes were applied (through a glaze applicator of 0.6 mm aperture) to porous tile bases for evaluation of their behaviour during firing. The pieces obtained were fired in a laboratory roller kiln at 1130 °C, in a 20-minute cycle. For colour evaluation (spectrophotometer Minolta CM 2600d) and evaluation of water mark, the pieces were left in contact with water for 15 minutes. Then a new colorimetric reading was made, thus determining the colour variation presented by the standard surface of the samples through the colorimetric parameter ΔE^*.

A part of the suspensions were dried in an electric oven and granulated with 7.0% water for pressing test specimens with 250 kgf/cm^2 compaction pressure. The apparent density and water absorption before firing and linear firing shrinkage were evaluated. A dilatometric test was performed from room temperature to 1000°C with a heating rate of 5°C/min.

(d) Experimental studies for glazes

A standard matte glaze (MS - STD) was formulated using wollastonite in its composition, which was replaced partially and totally by diopside, according to Table 5.

Raw material (%)	Composition of glazes		
	EM – STD	EM - 04	EM - 08
Kaolin MP002	11	11	11
Nepheline MP06/375	10	10	10
Quartz MP001	8	8	8
Zircon MP044	3	3	3
Frit FR016	12	12	12
Frit FR010	48	48	48
Wollastonite MP025	8	4	-
Diopside	-	4	8

Table 5. *Composition of glazes*

The compositions were milled in a laboratory mill with water equivalent to 44% of the total mass of the raw materials, 0.4% of sodium tripolyphosphate and 0.2% of carboxymethylcellulose. The densities of the suspensions obtained were determined in a pycnometer, whereas the apparent viscosities were determined with a Brookfield rotational viscometer at 30 RPM and estimated in the Ford cup No. 4. The residue content of the engobes was also determined by wet sieving in ABNT #325 sieve (45 µm aperture).

The glazes were then applied by a glaze applicator with 0.6 mm aperture to porous tile bases for evaluation of their behaviour during firing. The pieces obtained were fired in a laboratory roller kiln at 1130 °C, in a 20-minute cycle. The colour (spectrophotometer Minolta CM 2600d) and the brightness (in multimeter glossary Zehntner ZGM 1110, results of the reflections at 60°) were evaluated. The resistance to chemical attack was also evaluated for low concentration reagents according to the procedures of standard NBR 13.818, Annex H.

A part of the suspensions were dried in an electric oven and granulated with 7.0% water for pressing test specimens with 250 kgf/cm^2 compaction pressure. The dilatometric behaviour was evaluated from room temperature to the softening point of the glazes with a heating rate of 5 °C/min. High temperature viscosity tests were also carried out with cylindrical specimens with a diameter of 13 mm, fired on a sloping base at 45° for 10 minutes at 1130 °C.

5. RESULTS

The results of the experimental tests of the use of diopside in ceramic bodies of technical and glazed porcelain tiles, and in the composition of refractory and impermeable engobes and glazes are presented below.

(a) Results for technical porcelain tile

The behaviours of the ceramic bodies tested are illustrated as follows. Table 6 shows the results of the characterization of the suspensions and specimens before firing, prepared with each of the compositions. The vitrification curves of the compositions are presented in Figure 3, with indications of variations of water absorption and linear firing shrinkage as function of the firing temperature. Table 7 shows the characteristics of the fired bodies.

Characteristics	PT – STD	PT – 01	PT – 02	PT – 03
Slurry density (g/cm^3)	1.706	1.699	1.703	1.707
Residue > 45 µm (%)	1.3	1.2	1.7	1.4
Slurry viscosity – 30RPM (cP)	200	266	212	184
Flow time – Ford cup No. 4 (s)	56	61	55	46
Apparent density (g/cm^3)	1.81 ± 0.01	1.81 ± 0.01	1.81 ± 0.01	1.80 ± 0.01

Table 6. *Characteristics of ceramic bodies before firing*

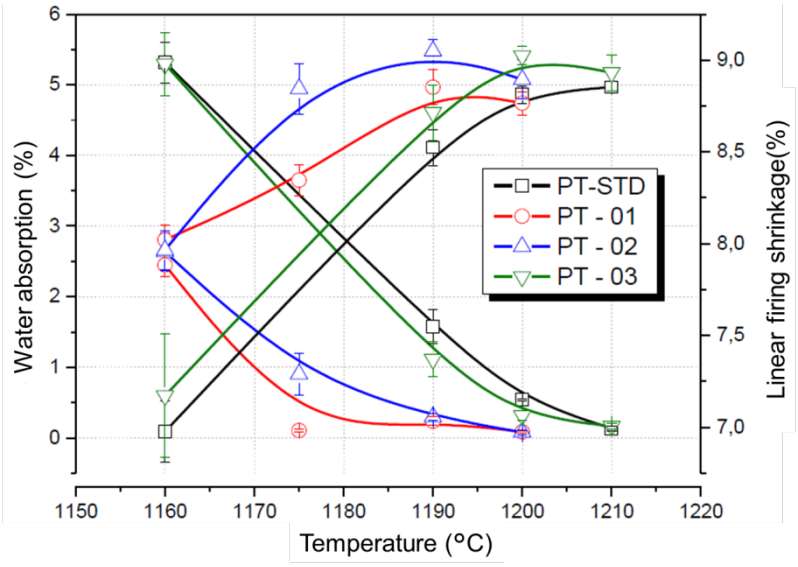

Fig. 3. *Vitrification curves of technical porcelain tiles*

Characteristics		PT – STD	PT – 01	PT – 02	PT – 03
Firing temperature (°C)		1210	1200	1200	1210
Water absorption (%)		0.14 ± 0.03	0.09 ± 0.02	0.08 ± 0.03	0.17 ± 0.04
Linear firing shrinkage (%)		8.9 ± 0.0	8.8 ± 0.1	8.9 ± 0.1	8.9 ± 0.1
L.O.I. (%)		5.6 ± 0.0	5.9 ± 0.1	5.7 ± 0.0	5.7 ± 0.1
Apparent porosity (%)		0.31 ± 0.08	0.20 ± 0.04	0.19 ± 0.07	0.38 ± 0.09
Density of fired body (g/cm3)		2.32	2.32	2.33	2.32
Flexural rupture modulus (MPa)		49 ± 5	57 ± 2	58 ± 2	50 ± 3
Pyroplasticity index (cm-1)		8.8 x 10-5	8.3 x 10-5	8.5 x 10-5	10.4 x 10-5
Chromatic coordinates	L*	78.8	73.6	75.7	81.0
	a*	1.3	2.3	1.7	0.7
	b*	7.2	8.5	8.2	7.9

Table 7. *Firing temperature and characteristics of technical porcelain tiles*

(b) Results for glazed porcelain tile

The behaviours of the porcelain tiles bodies tested are shown in the following illustrations. Table 8 shows the results of the characterization of the suspensions and specimens before firing, prepared with each of the compositions. The vitrification curves of the ceramic bodies are presented in Figure 4, with indications of variations of water absorption and linear retraction as a function of the firing temperature. Table 9 shows the characteristics of fired bodies.

Characteristics	PE – STD	PE – 02	PE – 05	PE – 10
Slurry density (g/cm³)	1.689	1.689	1.691	1.694
Residue > 45 µm (%)	7.2	7.2	7.1	7.4
Slurry viscosity – 30RPM (cP)	982	898	790	668
Flow time Ford cup No. 4 (s)	80	75	65	53
Apparent density (g/cm³)	1.94 ± 0.01	1.94 ± 0.01	1.96 ± 0.01	1.98 ± 0.01
Flex. rupture modulus (Kgf/cm²)	17 ± 1	18 ± 1	20 ± 2	34 ± 4
Linear drying shrinkage (%)	-0.04 ± 0.01	-0.05 ± 0.03	-0.13 ± 0.01	-0.12 ± 0.01

Table 8. *Characteristics of glazed porcelain tiles before firing*

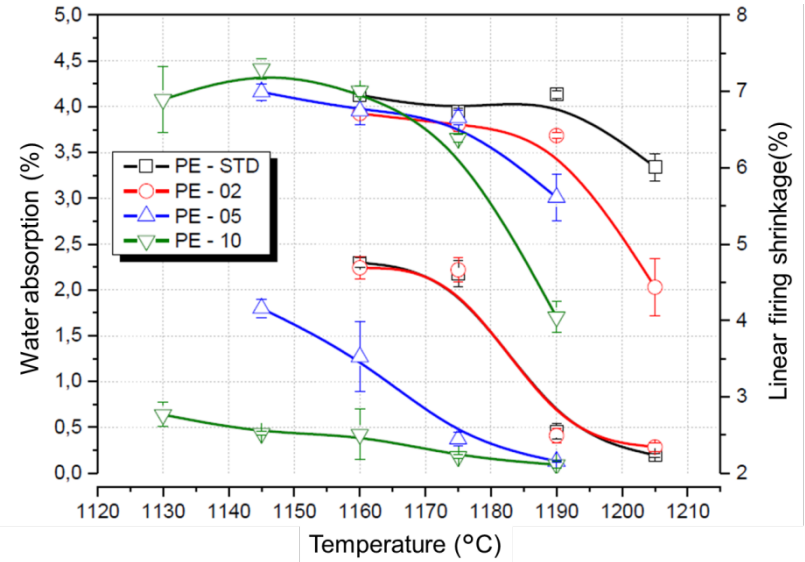

Fig. 4. *Vitrification curves for glazed porcelain tile bodies*

Characteristics		PE – STD	PE – 02	PE – 05	PE – 10
Firing temperature (°C)		1190	1190	1175	1145
Water absorption (%)		0.46 ± 0.09	0.41 ± 0.08	0.37 ± 0.07	0.43 ± 0.02
Firing linear shrinkage (%)		7.0 ± 0.0	6.4 ± 0.0	6.7 ± 0.1	7.3 ± 0.1
L.O.I. (%)		5.4 ± 0.1	5.2 ± 0.0	4.8 ± 0.1	4.9 ± 0.1
Apparent porosity (%)		1.07 ± 0.20	0.95 ± 0.18	0.88 ± 0.18	1.04 ± 0.05
Fired density (g/cm3)		2.35	2.32	2.38	2.40
Flexural rupture modulus (MPa)		41 ± 2	37 ± 2	46 ± 2	49 ± 3
Pyroplasticity index (cm-1)		7.2 x 10-5	10.0 x 10-5	7.3 x 10-5	9.1 x 10-5
Thermal exp. α 25–325(°C-1)		71.2 x 10-7	71.5 x 10-7	71.8 x 10-7	76.1 x 10-7
Chromatic coordinates	L*	59.7	59.3	58.3	58.5
	a*	1.1	0.8	1.7	2.8
	b*	11.7	11.1	12.4	13.4

Table 9. *Firing temperatures and characteristics of glazed porcelain tile bodies*

(c) Results for engobes

Table 10 shows the results of the determinations of density, viscosity, flow time and residue content of the slurry suspensions after discharge from the mills.

Table 11 presents the results of apparent density (Dap) of the specimens before firing, results of the characterization of the fired bodies, as well as the characteristics of the pieces. The graphs in Figures 6 to 10 illustrate the effects of diopside on the major properties of the engobes.

Characteristics	Impermeable engobe			Refractory engobe		
	EI-STD	EI-04	EI-08	ER-STD	ER-10	ER-20
Density (g/cm³)	1.845	1.829	1.818	1.801	1.809	1.816
Apparent viscosity (cP)	208	228	294	246	222	188
Flow time (s)	48	46	54	60	56	45
Residue 45 µm (%)	2.4	2.2	2.1	1.8	1.5	2

Table 10. *Characteristics of engobe slurries*

Characteristics		Impermeable engobe			Refractory engobe		
		EI-STD	EI-04	EI-08	ER-STD	ER-10	ER-20
Non-fired app. D (g/cm^3)		1.82±0.01	1.80±0.01	1.78±0.00	1.66±0.01	1.69±0.01	1.71±0.01
Water absorption (%)		5.8 ± 0.5	7.2 ± 0.8	6.2 ± 0.5	13.6± 0.8	14.7± 0.9	16.5± 0.2
Firing shrinkage (%)		6.7 ± 0.5	6.3 ± 0.2	6.5 ± 0.2	4.6 ± 0.1	3.5 ± 0.0	2.6 ± 0.1
L.O.I. (%)		2.2 ± 0.1	2.2 ± 0.0	2.1 ± 0.1	3.5 ± 0.1	3.1 ± 0.1	2.7 ± 0.1
Therm. exp.α25-325($°C^{-1}$)		$89.9x10^{-7}$	$88.7x10^{-7}$	$86.5x10^{-7}$	$107.7x10^{-7}$	$100.4x10^{-7}$	$106.7x10^{-7}$
Water mark (ΔE^*)		2	2.5	3.2	6.8	7.1	6.5
Chromatic coordinates	L*	92.3	91.6	90.6	92	92.5	93
	a*	0.8	0.8	1	1.5	1.4	1.3
	b*	2.6	2.7	2.8	4.5	4.2	4

Table 11. *Firing temperature and characteristics of fired engobes*

(d) Results for glazes

Table 12 shows the results of the determinations of density, viscosity, flow time and residue content of the glaze suspensions after mill discharge. The results of the characterization of the glazes are presented in Table 13, while the thermal expansion and digital images of the high temperature viscosity test are shown in Figs. 5 and 6, respectively.

Characteristics	EM – STD	EM – 04 (4% diopside)	EM – 08 (8% diopside)
Density (g/cm^3)	1.82	1.825	1.823
Viscosity apparent (cP)	864	472	320
Flow time (s)	n.d.a.	102	52
Residue 45 µm (%)	3.3	3.2	3

Table 12. *Characteristics of the glaze suspensions*

Characteristics		EM – STD	EM - 04	EM – 08
Thermal expansion coefficient - α 25-325 ($°C^{-1}$)		75.8×10^{-7}	75.8×10^{-7}	75.0×10^{-7}
Glass transition temperature - Tg (°C)		648	675	661
Softening temperature - Ta (°C)		765	790	774
Brightness – β 60° to 1160 °C ($\%_0$)		22.4	15.7	17.7
High temperature viscosity – length (mm)		15.0	13.4	13.2
Resistance to chemical attack	HCl 3%	GLA	GLA	GLA
	KOH 30 $g.L^{-1}$	GLA	GLA	GLA
	Citric acid	GLA	GLB	GLB
Chromatic coordinates	L*	86.9	87.8	88.5
	a*	2.1	1.8	1.6
	b*	5.6	4.1	3.6

Table 13. *Characterization of glazes*

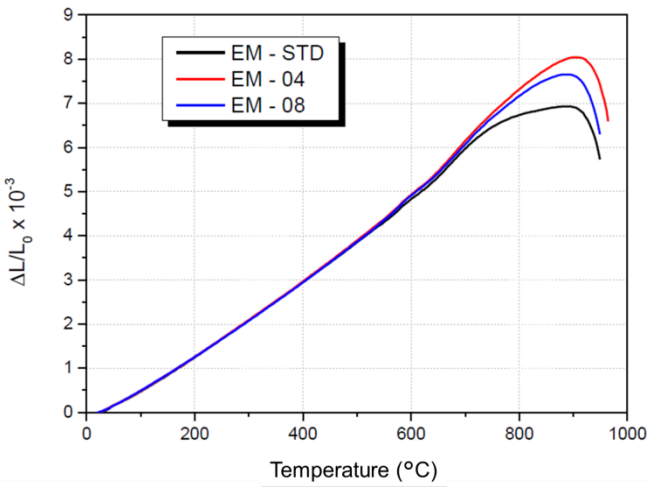

Fig. 5. *Thermal expansion of glazes*

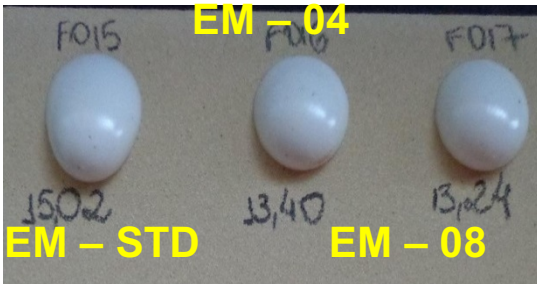

Fig. 6. *High temperature viscosity of glazes*

6. DISCUSSION AND CONCLUSION

The results are discussed according to its use in experiments, as follows:

Diopside in technical porcelain stone tile bodies

The best results were obtained with the PT-03 formulation, in which 5.5% of diopside totally replaced the talc and 50% of the zircon. The bodies presented whiter and less reddish colour compared to the standard formulation.

In the other analyses, no significant differences were observed between the PT-03 formulation and the PT-STD standard. There is only a slight reduction in the viscosity of the suspension, which is favourable for the atomization process, and an increase in the pyroplasticity index. The latter can be adjusted by slightly reducing the diopside content of the formula, which should not compromise its firing colour.

Based on these results, it can be stated that the use of diopside in technical porcelain tile bodies is technically feasible. It is believed that with some small adjustments in the formulation, better technical-economic performance can be obtained.

Diopside in glazed porcelain tile bodies

The test results indicate that incorporation of diopside in glazed porcelain tile bodies can bring significant advantages, especially with regard to the reduction of thermal energy consumption.

The presence of diopside in increasing content in glazed porcelain tile bodies produced significant reductions in the flow time of the suspensions. These results point to the possibility of increasing the solids concentration of the suspension to be atomized with the presence of diopside in the composition, which should reduce the consumption of gas for atomization of the slurry.

The most significant result was obtained during firing, where significant reductions in firing temperature of the porcelain tiles were evidenced as a function of the amount of diopside added. This effect is due to the probable formation of eutectic between the chemical elements contributed by diopside (calcium and magnesium) and the chemical elements present in phyllite and feldspar.

Other advantages worthy of note are related to the increases in mechanical strength of the dry bodies and their apparent density by the use of diopside in the body composition. These results, like the previous ones, are directly associated with the amount of diopside added in the composition.

In general, the other properties of porcelain tiles have undergone minor changes with the incorporation of diopside. The thermal expansion of the bodies only increased notably with the addition of 10% diopside. The small changes in colour of fired bodies are more associated with the reduction of the firing temperature for the ceramic body with higher levels of diopside.

The pyroplastic deformation naturally tends to increase slightly as a function of the above mentioned eutectic formation. However, the higher bulk density obtained by bodies containing diopside and the use of lower firing temperatures compensate for these differences, so that good results have been achieved especially by a body containing 5% diopside;

In view of the results obtained, it is suggested to use 3% to 5% diopside in glazed porcelain tile bodies so that the advantages discussed above are maximized.

Diopside in engobes

Experiments indicate that diopside can be used as a raw material for ceramic engobes, both in the composition of impermeable engobes and refractory ones;

In impermeable engobes, diopside can be used as a substitute for zirconium silicate, although in a rigorous analysis of the results some losses due to this substitution are observed.

As zirconium silicate is progressively replaced by diopside, small increases in water mark intensity and loss of whiteness are evident in the obtained engobes. These results are evidently less expressive in the partial substitutions performed and become more notable when the zircon is completely replaced.

In these compositions (impermeable engobes), there was also a reduction in the density of the suspensions and increase of the viscosity as a consequence of the replacement of zircon with diopside;

These results do not impair the use of diopside as a substitute for zircon in impermeable engobes. On the contrary, as the differences in behavior are relatively subtle and the economic advantages are considerable, it can be stated that diopside can be used as an excellent alternative for the substitution of zircon in this type of application.

In the case of refractory engobes, in which the effects of diopside addition on higher contents were evaluated, maintaining the proportion among the other raw materials, the main motivation for its use is the increase in the whiteness of the engobes. This result occurs without a simultaneous increase of the water mark, contrary to what usually occurs when refractory raw materials are incorporated in the engobes to make them whiter, as is the case of calcined kaolin and alumina.

In addition, with the application strategy tested with refractory engobes, the presence of diopside contributes to improving the rheological behaviour of the engobes, generating significant reductions of viscosity.

For the other properties evaluated, such as thermal expansion, no significant variations were observed in the results obtained by the diopside-containing engobes in comparison to the reference ones.

Diopside in glazes

The test results indicate that replacing wollastonite with diopside may be an alternative to harden matte glazes and increase their opacity, producing considerable gains in the rheological behaviour of the suspensions.

The results obtained indicated that glazes containing diopside present higher softening points, lower run-off at high temperatures and slightly lower brightness. These results were obtained without significant alterations in the thermal expansion of the glazes. Due to economic advantages deriving from the use of diopside in substitution of wollastonite, it is considered that this may be an alternative for the formulation of matte glazes.

The only negative aspect noted with the use of diopside in developed glazes was the reduction of chemical resistance against citric acid attack. Nevertheless, this is an acceptable result in accordance with regulatory tolerances, which can be conveniently adjusted by small changes in the final composition of the glaze.

7. AKNOWLEDGMENTS

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