STUDY OF THE INFLUENCE OF ADDING CALCINED ALUMINAS TO PORCELAIN TILE COMPOSITIONS

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ABSTRACT

Compared with other types of ceramic tiles, porcelain tile is characterised by very high density, which provides it with excellent characteristics as regards bending strength, resistance to surface abrasion, stain resistance, surface hardness and relatively high fracture toughness. Porcelain tile differs from other types of ceramic tile due to its highly technological production process, involving firing in fast cycles at temperatures from around 1200 to 1250°C. The optimum properties of this product are due to the high quality of the compositional raw materials, high degree of milling, large quantity of fluxes and high compaction force.

The challenge of manufacturing porcelain tile starts in the selection of the raw materials. Control of raw materials is essential to maintaining homogeneity and avoiding variations in the fusibility of the composition.

The main objective of this work has been to evaluate the influence of the addition of several types of calcined aluminas with different surface areas, quantity of sodium and quantity of alpha phase, to industrial porcelain tile compositions.

The chemical and physical properties of the individual raw materials were studied and 34 different porcelain tile compositions were evaluated. The following properties and characteristics were evaluated: suspension rheological behaviour as a function of the alumina additions, crystalline phases present after firing, firing shrinkage, water absorption, apparent and closed porosity, mechanical strength, abrasion resistance, chemical resistance and final microstructure of the test specimens. The action of the aluminas in contact with highly fluxing raw materials was also studied.

1. THE PORCELAIN TILE MARKET

World production of porcelain tile has increased progressively in recent years. At the moment, the volume of porcelain tile production in Italy already accounts for 54.4% of total Italian ceramic tile production. Following the trend, Spain and Brazil are also working on this type of tile, increasing their installed capacity and developing production technologies. The technical characteristics of the porcelain tiles made in Brazil are comparable to those of Italian products, which are considered to be quality leaders by world markets.

Table 1 details Italian porcelain tile production, showing highly expressive growth. Glazed porcelain tile displays a high rate of growth compared with the unglazed product.

Description	Millions of m^2					
	1997	1998	1999	2000	2001	2002
Unglazed porcelain tile	102.6	120.8	127.8	143.3	147.6	140.4
Glazed porcelain tile	24.7	56.1	90.7	125.2	161.1	188.8
Total porcelain tile	127.3	176.8	218.5	268.5	308.7	329.2

Table 1. Italian porcelain tile production (In Ceramic World Review)

Analysis of Spanish porcelain tile production (Table 2) also shows growth, though not to the same extent as in Italy. In 2001, porcelain tile production reached 7.2% of total Spanish ceramic tile production, which is very low compared with Italy (54.4%).

Description	Production (million of m^2)						
	1995	1996	1997	1998	1999	2000	2001
Porcelain tile	13.8	14.1	16.5	24.0	29.8	34.4	45.9

Table 2. Porcelain tile production in Spain. (In ASCER)

When Brazilian porcelain tile production of recent years is evaluated, gradual growth is also observed. In 2000, Brazilian porcelain tile production was estimated at 4 million m^2, accounting for 0.9% of total tile production. Now in 2003, the present monthly production of porcelain tile is estimated at 1,445,000 m^2/month (Table 3), around three times the monthly production of 2000. At the moment, the companies that produce this type of product in Brazil are: Cecrisa (MG), Portobello (SC), Eliane (SC), Elizabeth (PB), Ceusa (SC), Itagrês (SC), Chiarelli (SP), Gyotoku (SP) and Unigrês (SP). Present Brazilian installed capacity for porcelain tile production is 2,120,000 m^2/month (Table 4). The present national production of porcelain tile is divided into two types: unglazed (technical) porcelain tile with a monthly production of 885 thousand m^2, and glazed porcelain tile with a monthly production of 570 thousand m^2. If this rate of production is maintained until the end of 2003, Brazil will foreseeably reach an annual production of 17 million m^2, i.e., around 3% of total Brazilian tile production.

Company	Production (m^2/month)		
	Technical porcelain tile	Glazed porcelain tile	Total
Cecrisa	140,000	50,000	190,000
Itagrês	-	40,000	40,000
Ceusa	25,000	15,000	40,000
Elizabeth	130,000	20,000	150,000
Chiarelli	-	100,000	100,000
Portobello	300,000	300,000	600,000
Gyotoku	50,000	20,000	70,000
Unigrês	-	25,000	25,000
Eliane	240,000*	**	240,000*
Total	885,000	570,000	1,445,000

**Estimated, **Not known*

Table 3. Current monthly Brazilian porcelain tile production in terms of product type.

Company	Installed capacity (m^2/month)
Cecrisa	360,000
Itagrês	150,000
Ceusa	60,000
Elizabeth	150,000
Chiarelli	150,000
Portobello	900,000
Gyotoku	70,000
Eliane	280,000*
Total	2,120,000

**Estimated*

Table 4. Current Brazilian installed monthly capacity of porcelain tile production.

The Cecrisa porcelain tile factory is located in the State of Gerais Mines in Brazil, and its main lines of unglazed products are: Marmi, Colori (plain colours), Graniti (salt and pepper) and Geo. The main sizes made are: 30X30, 45X45, 45X90, 60X60, 60X120 cm. Figure 1 displays some examples of products manufactured by this company.

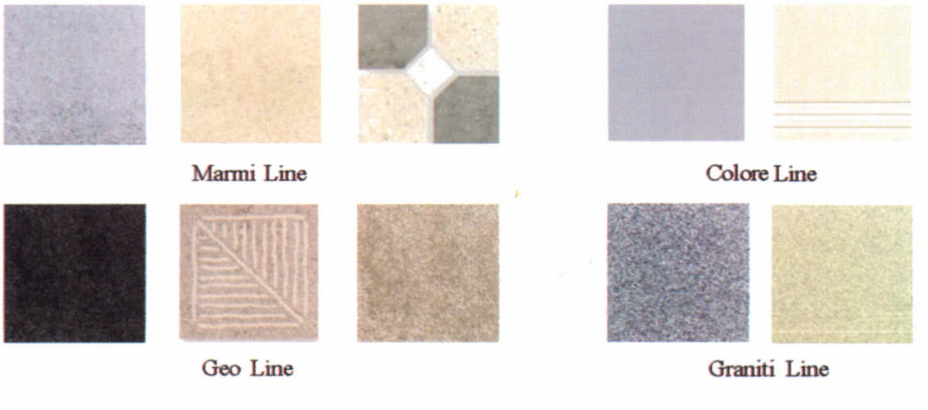


Figure 1. Some examples of products manufactured by Cecrisa. (Source: www.cecrisa.com.br)

The Portobello porcelain tile factory is located in the South State in Brazil and its main lines of unglazed products are: Galleria D'Arte, Pietra Naturale, Série Travertinos, Série Venato, Série Granito, Série Progetto, while the lines of glazed products are: Série New Age, Série D'Ampezzo, Série Logwood, Série Jerusalém, Série Bahia, Série Vintage and Série Pedra da Gávea. The main sizes made in unglazed products are: 60X120, 60X60, 45X45, 30X60, 30X30 cm, and in glazed products: 45X45, 30X60, 30X30, 15X15, 05X15, 7.5X7.5, 10X10. Figure 2 displays some examples of products manufactured by this company.

Figure 2. Some examples of products manufactured by Portobello. (Source: www.portobello.com.br)

The Elizabeth porcelain tile factory is located in the northeast of Brazil and its main lines of unglazed products are: Antique, Atlantis, Colore, Dolomiti, Duna, Graniti, Ibiza, Lagui, Mediterráneo, Tambaú, Vulcano. The main size made is 40X40 cm. Figure 3 displays some examples of products manufactured by this company.

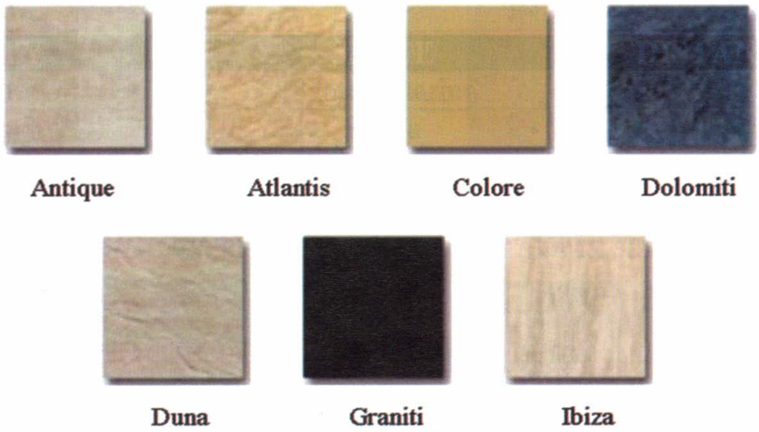


Figure 3. Some examples of products manufactured by Elizabeth. (Source: www.ceramicaelizabeth.com.br)

The Gyotoku porcelain tile factory is located in the State of São Paulo in Brazil, and its main lines of unglazed products are: Shine Line, Shine Square, Progetto, Reale, Dakar, Vesúvio. The main sizes made are 40X40, 40X20 and 20X20 cm. Figure 4 displays some examples of products manufactured by this company.

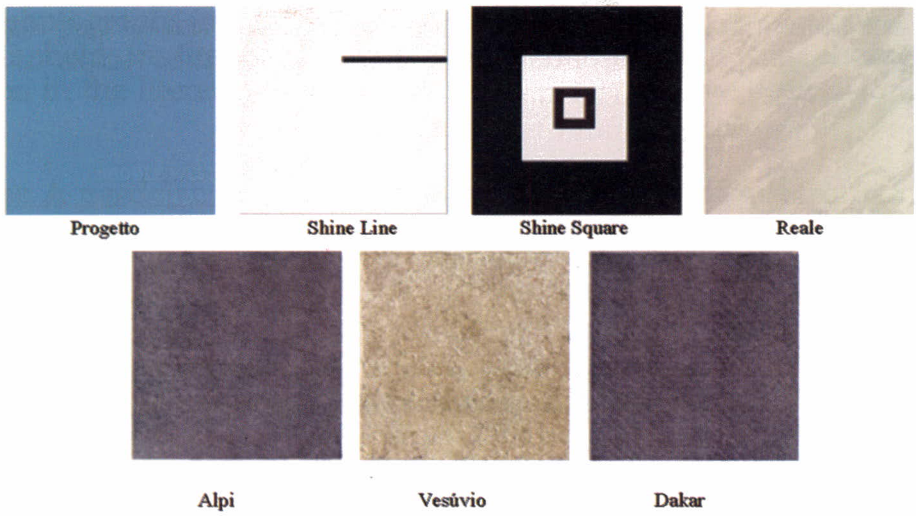


Figure 4. Some examples of products manufactured by Gyotoku. (Source: www.gyotoku.com.br)

The Chiarelli porcelain tile factory is located in the State of São Paulo in Brazil, and its main lines of glazed products are: Porfido, Etrusco, Pietra Lunari. The main sizes made are 43X43, and 34X34 cm. Figure 5 displays some examples of products manufactured by this company.

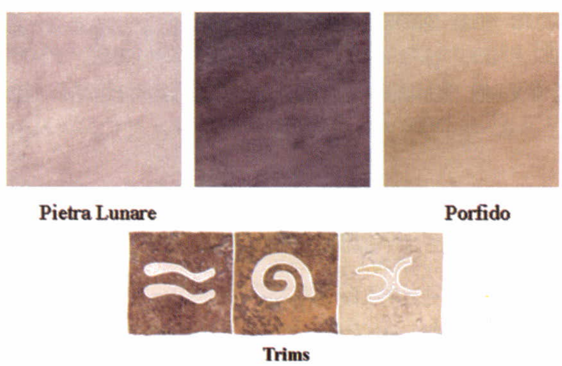


Figure 5. Some examples of products manufactured by Chiarelli.

The Itagres porcelain tile factory is located in the State of Santa Catarina in Brazil, and its main lines of glazed products are: Arena, Arezzo, Fiorano, Livorno, Montalcino, Naturale. The main sizes made are 33.5X33.5 and 41.6X41.6 cm. Figure 6 displays some examples of products manufactured by this company.

Figure 6. Some examples of products manufactured by Itagrês. (www.itagres.com.br)

The Ceusa porcelain tile factory is located in the State of Santa Catarina in Brazil, and their main lines of glazed products are: Sabará and Romano, while the main line of unglazed products is Stone. The main size made is 42.5X42.5 cm. Figure 7 displays some examples of products manufactured by this company.

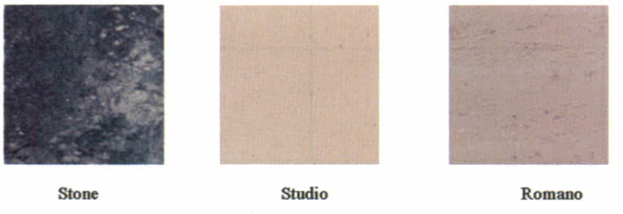


Figure 7. Some examples of products manufactured by Ceusa. (www.ceusa.com.br)

In view of the importance and growth of porcelain tile production in Brazil, the present work was undertaken to study the influence of the addition of different types of calcined alumina, with different surface areas, quantity of alpha phase and quantity of sodium in industrial porcelain tile compositions.

2. EXPERIMENTAL PROCEDURE

The calcined aluminas used in the work were: A-1, A-2, P-900 and A-50. The chemical characterization, surface area, particle size distribution and quantity of alpha phase of each alumina are given in Table 5.

Alumina		A-1	A-2	P-900	A-50
Chemical analysis	Al_2O_3 (%)	98.6	99.3	99.2	86.8
	SiO_2 (%)	0.021	0.023	0.021	0.044
	Fe_2O_3 (%)	0.029	0.031	0.030	0.028
	Na_2O (%)	0.43	0.44	0.44	0.50
	CaO (%)	0.025	0.029	0.029	0.016
	MnO (ppm)	19	21	1	13
Surface area (m^2/g)		64	1.3	7	52
Moisture content	LOI (%)	0.58	0.03	0.06	5.11
	U300 (%)	0.31	0.10	0.21	7.47
Particle size distribution	+100# (%)	2	4	3	-
	+200# (%)	62	58	52	-
	+325# (%)	95	92	91	5
Mean particle size	D_{10} (μm)	52	44	44	3
	D_{50} (μm)	88	87	83	11
	D_{90} (μm)	140	143	139	36
Quantity of alpha phase	(%)	5	95	50	40

Table 5. Data on the calcined aluminas used in the study.

Table 6 presents the studied porcelain tile formulations. Formulation A without any alumina addition was a standard industrial composition (STD).

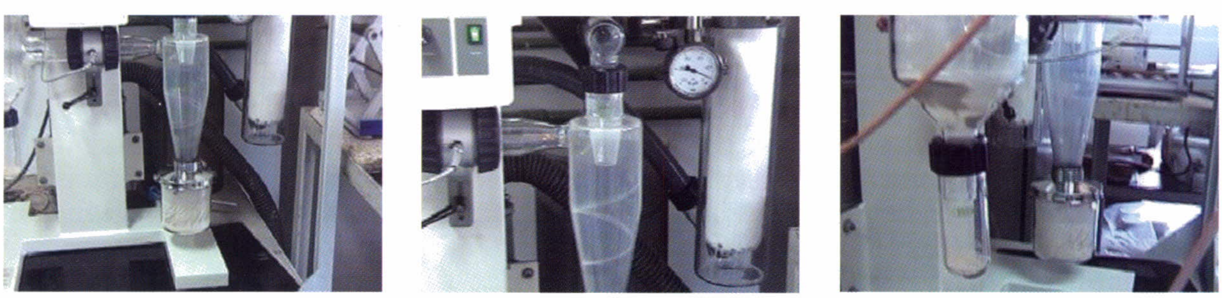
Raw material	Formulations (% by weight)							
	Test 1		Test 2			Test 3		
	A	B	C	D	E	F	G	H
MP-38	5	5	4	3	2	5	5	5
MP-55	6	6	6	6	6	6	6	6
MP-05	10	10	10	10	10	9	8	7
MP-08	14	14	14	14	14	14	14	14
MP-60	1	1	1	1	1	1	1	1
MP-64	14	14	14	14	14	14	14	14
MP-62	20	20	20	20	20	20	20	20
MP-63	30	30	30	30	30	30	30	30
Boric acid	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sodium silicate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
A-1 A-2 P-900 A-50	1	2	1	2	3	1	2	3

Table 6. Studied porcelain tile formulations.

Three modes were evaluated of adding alumina to the porcelain tile composition:

- **TEST 1:** Alumina addition as an additive (above 100% of the formulation): Formulation A: 1% and Formulation B: 2%
- **TEST 2:** Alumina addition replacing a raw material rich in quartz (MP 38): Formulation C: 1%, Formulation D: 2% and Formulation E: 3%
- **TEST 3:** Alumina addition replacing a raw material rich in kaolin (MP05): Formulation F: 1%, Formulation G: 2% and Formulation H: 3%.

Mixing and milling of the compositions were conducted at the Laboratory of Applications of Alcoa Alumínio S.A. The ball mill used had a capacity for 5 kg suspension. The solids/water ratio was 58/42 %. The milling media used were high alumina. The milling time was established based on a reject of 1.5-2 g on a 250 mesh. Spray drying was performed in a laboratory spray dryer in accordance with Figure 8.



Fines collector *Detail of the cyclone* *Detail of the fines collector*

Figure 8. Spray-drying process of the studied compositions.

Compaction was performed using steel dies of 2X 7 cm^2. The pressure set was 5.6 ton to obtain a density after compaction of 2 g/cm^3.

Firing was conducted in a laboratory kiln, using the following curve: to 500°C: 95°C/min; from 500°C to peak firing temperature: 25°C/min; residence at peak temperature: 6 minutes; cooling: 50°C/min.

After firing we evaluated: bulk density, theoretical density, apparent, closed and total porosity, water absorption, breaking load, bending strength, linear firing shrinkage.

The next phase of the work was to select the compositions that presented the best results: A-A50, B-A50, E-A2 and G-A2. After milling the suspensions, the following were determined: measurement of the reject on mesh 250, measurement of viscosity in a Brookfield digital viscometer and measurement of suspension density. Chemical analysis was performed by X-ray fluorescence and X-ray diffraction of the compositions. The vitrification curve was determined at 6 temperatures: 1200, 1210, 1220, 1225, 1230 and 1240°C. The firing temperature used was 1225°C, and the same firing curve mentioned above was used. The following end product characterizations were conducted: breaking load, bending strength, bulk density, apparent, closed and total porosity, resistance to deep abrasion, resistance to chemical attack, stain resistance and microstructural analysis.

The presence of the aluminas in the development of the viscous phase during sintering and final microstructure of the porcelain tile was also studied. The objective of this study phase was to determine how the added alumina particles of A-1, A-2, P-900 and A-50 would remain in the end product microstructure, and how this might affect final product properties.

As the porcelain tile densification process mainly occurs by sintering in the presence of viscous flow, and as the this last phase is the most reactive, providing the most significant transformations for achieving a final dense body, the methodology was adopted of identifying the raw materials of the STD formulation, with the greatest fluxing potential to study their reactivity.

Two formulations containing the fluxing raw materials and aluminas were then studied, keeping their proportions by weight according to the original composition. The studied compositions are given in Table 7. Composition C^{I} was selected, because it contained the mixture of raw materials with the greatest fluxing power. Formulation C^{II} consisted of all the raw materials that might possibly form viscous flow in the porcelain tile formulation and included the raw materials present in C^{I}.

All the raw materials listed in Table 7 were ground in a revolving mill until obtaining a reject of around 2% on mesh ABNT No. 325. Fusion test specimens were made of all the compositions, with a base diameter of 3.5 cm and height of approximately 40.0 cm, using the process of fusion in a gypsum mould.

The fusion test specimens were subjected to heat treatment at the respective temperatures: 1215, 1220, 1225 and 1230°C. The firing curves used, cold to cold, lasted between 35 and 40 minutes, in which the test specimens were held for 4 minutes at firing peak temperature. For this a fast-firing laboratory kiln was used.

The main data obtained were bulk density and water absorption after firing, linear shrinkage in test specimen diameter and height, loss on ignition and abrasion resistance. We also ran microanalysis (energy-dispersive X-ray spectroscopy, EDS) of images obtained by scanning electron microscopy (SEM) of the test specimens after heat treatment, to identify the distribution form of the element aluminium.

	Raw materials	% (by weight)		Selection criterion
		STD composition	Alumina-containing compositions	
IDENTIFICATION		$C^{I\text{-}Ref}$	$C^{I\text{-}A1,\text{-}A2,\text{-}P900,\text{-}A50}$	Compositions containing materials with greater fluxing power in the porcelain tile formulation
C^{I}	MP 63	59.06	59.06	
	MP 62	39.37	39.37	
	Boric acid	1.57	1.57	
	Alumina	----	**2.00**	
IDENTIFICATION		$C^{II\text{-}Ref}$	$C^{II\text{-}A1,\text{-}A2,\text{-}P900,\text{-}A50}$	Compositions containing all the raw materials identified as having some fluxing power in the porcelain tile formulation
C^{II}	MP 63	42.37	42.37	
	MP 62	28.26	28.26	
	MP 38	7.06	7.06	
	MP 60	1.41	1.41	
	MP 64	19.77	19.77	
	Boric acid	1.13	1.13	
	Alumina	----	2.00	

Table 7. Studied compositions with the addition of aluminas: A-1, A-2, P-900 and A-50.

3. RESULTS AND DISCUSSION

Table 8 lists the characteristics of the raw materials used in the study.

Chemical analysis	% by weight							
Compounds	MP55	MP62	MP08	MP05	MP38	MP63	MP60	MP64
SiO_2	65.76	75.86	59.82	62.41	70.32	80.74	46.13	43.18
Al_2O_3	0.76	14.49	26.08	24.18	16.44	10.42	20.73	37.63
Fe_2O_3	0.26	0.07	1.14	1.08	0.99	0.08	0.83	2.02
CaO	0.29	0.34	0.04	0.02	0.04	0.11	7.62	0.03
Na_2O	<0.01	7.94	0.12	0.10	0.05	1.53	0.55	0.16
K_2O	<0.01	0.45	1.16	0.70	5.57	6.73	4.45	3.28
MnO	0.05	<0.01	0.01	0.01	<0.01	<0.01	0.13	0.02
TiO_2	0.02	0.04	1.24	1.17	0.67	<0.01	0.07	1.09
MgO	27.38	<0.01	<0.01	<0.01	2.35	<0.01	3.94	<0.01
P_2O_5	0.06	0.05	0.11	0.10	0.08	0.06	0.24	0.18
LOI	5.22	0.75	10.29	10.23	3.47	0.33	15.31	12.43
Surface area	9.8	7.0	21.2	22.3	12.9	7.8	11.7	22.3
Mineralogical analysis	Talc, quartz and calcite	Quartz, sodium and potassium feldspar, illite	Kaolinite, mica, potassium feldspar, gibbsite	Kaolinite, illite, quartz and potassium feldspar	Kaolinite, quartz and mica	Kaolinite, potassium and sodium feldspar, quartz	Calcite, kaolinite, dolomite	Kaolinite, mica, gibbsite, quartz

Table 8. Characteristics of the raw materials used in the study.

First the 34 porcelain tile compositions with the addition of four types of alumina (in accordance with Table 6) were characterized. The effects of the alumina additions were as follows:

- Where alumina was added as an additive (above 100%), compositions A and B, the best results for bending strength and breaking load were obtained for aluminas A-50 and A-2. A-1 alumina, as an additive, lowered mechanical properties compared with the STD composition. The addition of aluminas A-50 and A-2 did not affect the values of apparent porosity, but alumina A-50 produced a lower closed porosity than the STD composition.
- Where alumina was added replacing a raw material rich in quartz, compositions C, D and E, only A-2 alumina raised mechanical strength. Regarding closed porosity, aluminas A-50 and A-2 lowered these values. Adding A-1 alumina reduced bending strength and breaking load, and increased apparent porosity.
- Where alumina was added replacing a raw material rich in kaolinite, compositions F and H, A-2 alumina improved bending strength and breaking load. Aluminas A-2 and P-900 increased closed porosity. Alumina A-1 raised apparent porosity and reduced closed porosity.

In view of the preliminary results, a selection was made of the compositions that displayed the best results: A-A50, B-A50, E-A2 and G-A2. Figure 9 shows the viscosity of the studied suspensions. Adding alumina A-50 as an additive increased suspension viscosity, and the addition of alumina A-2 replacing quartz and kaolinite led to a small decrease in suspension viscosity. Figures 10, 11 and 12 plot mechanical strength, water absorption and apparent porosity versus the firing temperature used in defining optimum firing conditions.

Table 8 lists the results of chemical analysis by ray-X fluorescence of the studied compositions (after firing). It can be observed that the compositions exhibit a greater amount of aluminium oxide, a greater amount of CaO, and smaller amounts of Na_2O, K_2O and MgO. X-ray diffraction analysis indicated that the studied compositions contained the phases quartz and mullite.

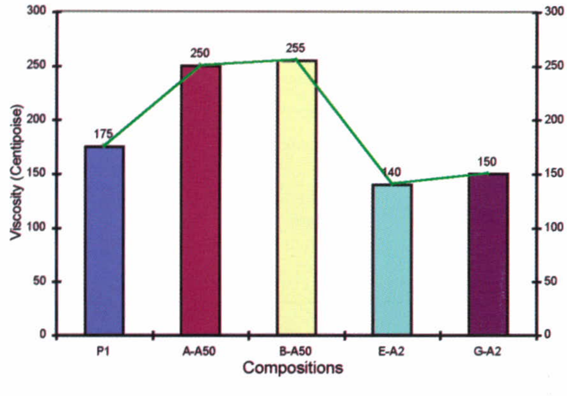


Figure 9. Viscosity of the studied porcelain tile compositions.

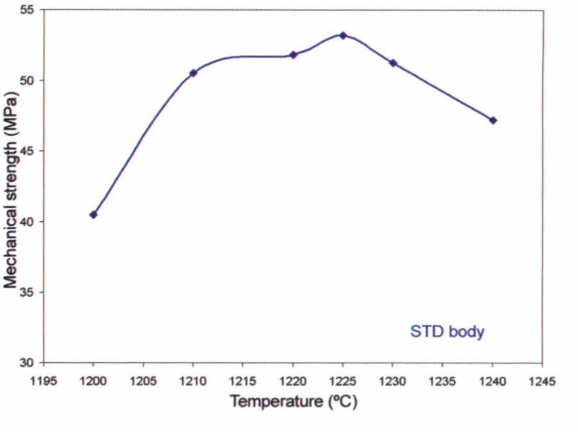


Figure 10. Mechanical strength values versus firing temperature of the STD composition.

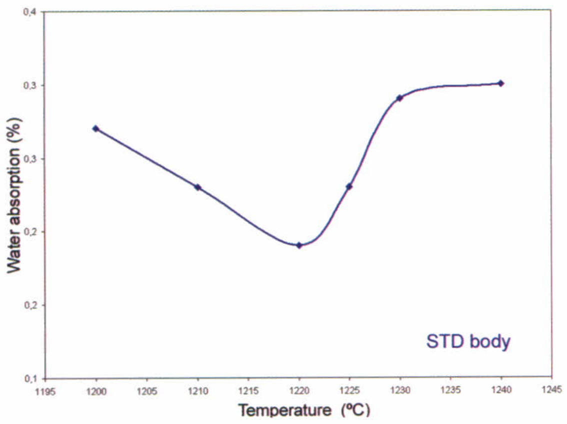


Figure 11. Water absorption values versus firing temperature of the STD composition.

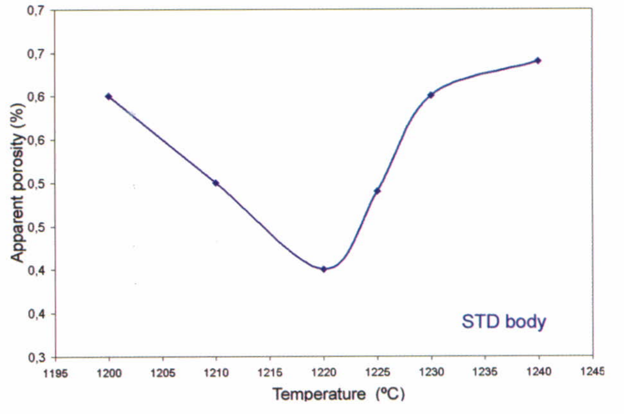


Figure 12. Bulk density values versus firing temperature of the STD composition.

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MnO	TiO_2	MgO	P_2O_5	LOI
STD	69.90	19.70	0.64	0.24	2.37	4.06	0.01	0.53	1.55	0.05	0.97
A-A50	68.49	21.41	0.72	0.21	2.28	3.98	<0.01	0.55	1.60	0.05	0.71
B-A50	68.17	22.26	0.67	1.79	2.06	2.57	0.01	0.48	1.24	0.05	0.69
E-A2	66.95	23.15	0.63	0.21	2.28	3.75	<0.01	0.53	1.54	0.05	0.92
G-A2	68.15	21.54	0.61	0.21	2.31	3.99	0.01	0.51	1.53	0.05	1.09

Table 8. Results of chemical analysis by X-ray fluorescence of the studied compositions.

Table 9 details the mechanical and physical properties of the studied porcelain tile compositions. The addition of 1% A-50 alumina to the STD composition led to an increase of around 9% in bending strength and breaking load, though it produced a higher total porosity than the STD composition. The addition of 2% A-50 alumina lowered all mechanical properties and also produced higher closed porosity than the STD composition, as well as greater water absorption. This high closed porosity was probably responsible for the reduction in mechanical strength. As A-50 alumina had high LOI (owing to the presence of aluminium hydroxide), it released bubbles in firing, and as the firing rate was fast, there was not enough time to eliminate the bubbles. This high closed porosity can significantly affect the stain resistance of the products, hampering cleaning.

The A-2 alumina addition replacing a raw material rich in quartz increased mechanical properties, but also produced higher closed porosity, which could affect product cleaning properties.

Introducing A-2 alumina as a replacement for a raw material rich in kaolinite caused a significant rise in mechanical properties, as well as a reduction in total and closed porosity.

Properties	P1	A-A50	B-A50	E-A2	G-A2
Thickness (mm)	8.62	8.63	8.58	8.54	8.76
BL (N)	2448±237	2675±137	2111±69	3488±248	2960±186
MOR (MPa)	49.4±2.6	53.9±2.9	43.0±1.4	71.6±4.7	58.0±5.0
$BL_{Min\ STD\ value}$	2024	2478	2037	3126	2724
$MOR_{Min\ STD\ value}$	44.9	50.62	40.93	65.35	52.0
$\rho_{theoretical}$ (g/cm^3)	2.50	2.51	2.51	2.51	2.51
PA (%)	0.15	0.14	0.32	0.13	0.10
PF (%)	3.70	5.50	7.40	5.86	2.24
PT (%)	3.85	5.64	7.72	5.99	2.34
WA (%)	0.07	0.06	0.14	0.06	0.04

Table 9. Mechanical and physical properties of the studied porcelain tile compositions.

Table 10 details the values of deep abrasion resistance of the porcelain tile compositions. It can be observed that the alumina addition provided a significant increase in deep abrasion resistance, particularly compositions A-50 and G-A2.

Composition	Mean value		Maximum value (mm^3)
	Cord length (C_{CORD}) (mm)	Volume of material removed (V) (mm^3)	
STD	26.3 ± 1.1	160.9 ± 21.8	176.3
A-A50	22.8 ± 0.9	103.6 ± 14.2	113.6
B-A50	23.6 ± 0.5	113.1 ± 9.3	119.6
E-A2	23.8 ± 0.6	118.3 ± 8.5	124.3
G-A2	22.7 ± 0.7	100.1 ± 11.3	108.2

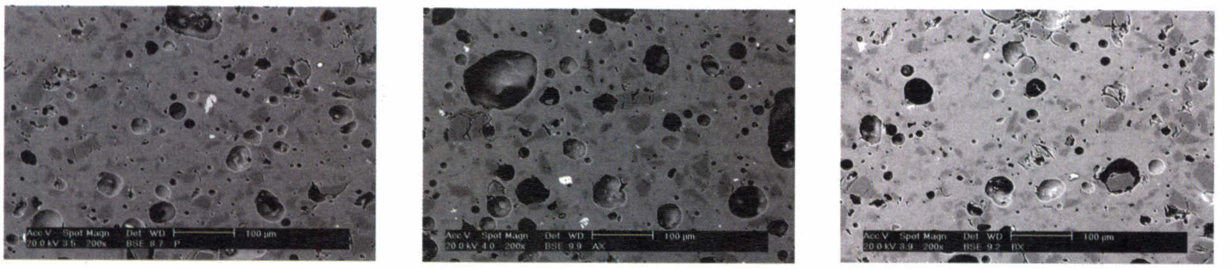
Table 10. Values of chord length and volume of material removed from the porcelain tile compositions.

All the products displayed class A resistance to chemical attack, even to low and high concentration basic and acid products. Table 11 presents a summary of the stain resistance results of the studied compositions (polished test specimens). All the test specimens displayed low stain resistance. It is important to note that no surface sealer was applied before the test. The polished products that are marketed generally have a sealing layer that fills the surface pores and consequently raises stain resistance. Applying a surface sealer would probably lead to better stain resistance results in the test compositions.

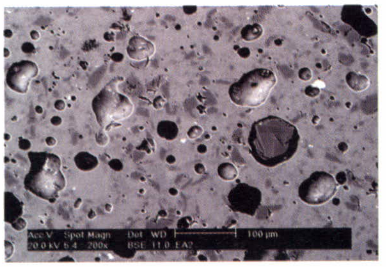
Composition	Staining agents		
	Chromium green (penetrating agent)	Olive oil (film forming agent)	Iodine in alcohol solution (oxidizing agent)
STD	1	1	1
A-A50	1	1	1
B-A50	1	1	1
E-A2	1	1	1
G-A2	1	1	1

Class 1: Impossibility of stain removal.
Table 11. Results of the stain resistance of the studied porcelain tile compositions.

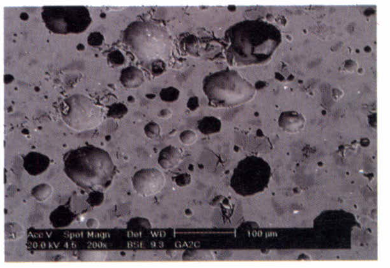
Figure 13 compares all the SEM images (magnification 200x) of the studied samples. They all exhibited a rise of closed porosity with the alumina addition.



(a) STD body *(b) A-A50* *(c) B-A50*



(d) E-A2



(e) G-A2

Figure 13. SEM images (magnification 200x) of samples of the studied porcelain tile compositions.

The study of the influence of the presence of alumina on the development of the viscous phase during sintering was conducted to determine how the alumina particles altered end product microstructure. Composition C^{I} was selected, because it contained the raw materials mixture with the greatest fluxing power. Formulation C^{II} consisted of all the raw materials that might form viscous flow in the porcelain tile formulation, including the raw materials present in C^{I}. The water absorption results obtained for the test specimens after firing are displayed in Figures 14 and 15. Composition C^{I} containing the most vigorous fluxes exhibited gradual vitrification in the evaluated temperature range, and at around 1215°C, test specimens were obtained with even higher values of water absorption, between 3 and 7%. Across the entire range of test temperatures, the test specimens of composition C^{II} displayed water absorption lower than 0.25%, indicating that the liquid phase that forms with this mixture of raw materials provides more efficient vitrification, probably due to a greater amount of liquid phase with a lower viscosity than that of composition C^{I}. This occurs due to the presence of compounds with low melting points, which form at the interparticle contact points, enabling the formation, by a process of fusion at lower temperature, of a liquid that encourages the porcelain tile densification process.

Table 12 details the microstructures and corresponding aluminium scans for composition C^{II}. It also sets out the STD sample composition ($C^{II\text{-}STD}$), the sample composition with the alumina addition of the greatest surface area ($C^{II\text{-}A50}$), and the composition with the alumina of the smallest surface area ($C^{II\text{-}A2}$). The data show that the alumina addition produced a gain in deep abrasion resistance. This implies a porcelain tile consisting of a more resistant glassy phase owing to the alumina addition, which can occur separately in two ways:

- Solubility of alumina particles in the molten glassy phase composition, yielding a final microstructure with a glassy phase rich in Al_2O_3 and, therefore, with greater hardness;

- Insolubility of the alumina in the viscous flow, in which the particles act as strengtheners in the formation of a composite with a glassy matrix/crystalline strengthening.

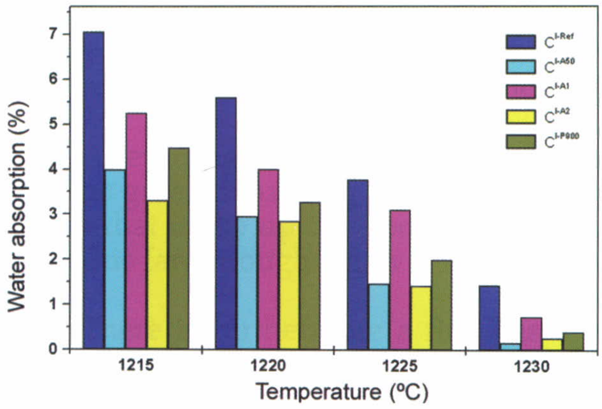


Figure 14. Water absorption values obtained for C^{I}.

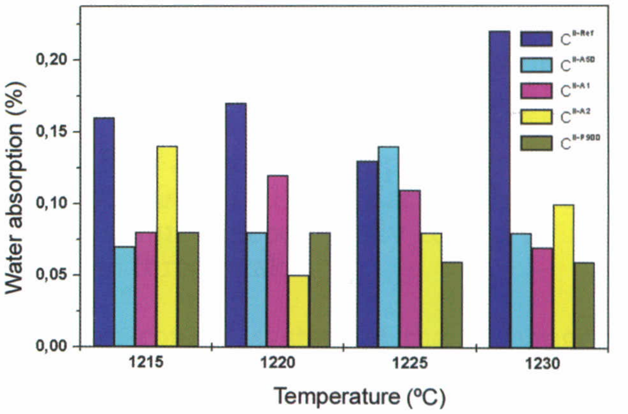
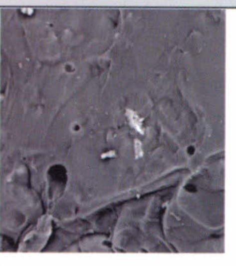
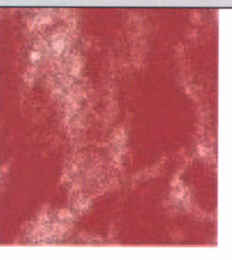
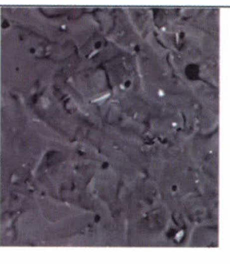
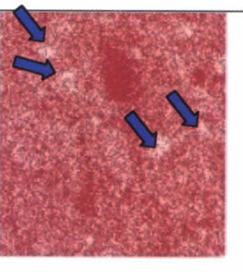
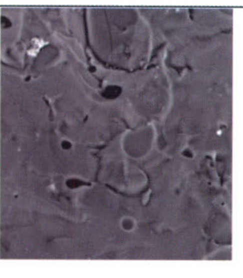
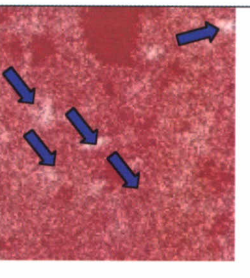


Figure 15. Water absorption values obtained for C^{II}.

Sample	SEM IMAGE	ALUMINIUM SCAN	OBSERVATIONS
C^{II-STD}			$\%Al_2O_3$ (weight) = 7.58 % V=140.15 mm^3 **(*without alumina addition*)**
C^{II-A2}			$\%Al_2O_3$ (weight) = 9.56 % V=121.91 mm^3 **(*2% A2 alumina addition with $A_{surface}$=1.4 m^2/g*)**
C^{II-A50}			$\%Al_2O_3$ (weight) = 9.28 % V=125.88 mm^3 **(*2% A50 alumina addition with $A_{surface}$=50 m^2/g*)**

** V = volume material removed from the abraded track*
Table 12. Aluminium scans (energy-dispersive X-ray spectroscopy) in samples C^{II}.

In Table 12, the blue arrows indicate the insoluble alumina particles in the glassy matrix. A greater quantity of remaining particles was observed in the test specimens that contained A-2 alumina. Independently of the type of alumina, the abrasion resistance of the glassy phase increased. Analysis of Table 12 indicates that the greater alpha phase content of A-2 alumina causes lower dissolution in the melt, giving rise to crystals scattered throughout the glassy phase. These crystals act as catalysts for mullite formation, providing the products with better mechanical and abrasion resistance.

However, special care needs to be taken so that the presence of a greater quantity of aluminium in the glassy matrix is not exaggerated, to avoid raising porosity of the product. The glasses that contain alumina are known for their good mechanical properties, but it is also common for exaggerated proportions to raise the viscosity of the glassy phase.

4. CONCLUSIONS

This study has shown that adding calcined aluminas can lead to a significant improvement of the mechanical and physical properties of porcelain tile compositions. The alumina that provided the most significant improvements in the end product properties was the A-2 type. This alumina has a high quantity alpha phase, which probably acts as a catalyst for mullite formation. Alumina A-50 can be added in small amounts, because it has high loss on ignition due the presence of aluminium hydroxide, which during firing releases gases, maintaining closed porosity.

The study has also indicated that the alumina addition can be done in two ways: as an addition or by replacing a raw material rich in kaolinite.

5. ACKNOWLEDGEMENT

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