MANUFACTURE OF PORCELAIN TILE WITH SELECTED RAW MATERIALS FROM THE ARGENTINE REPUBLIC

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1. INTRODUCTION

Porcelain tile is a material sintered in the glassy phase with excellent technical performance features as a ceramic body. In aesthetic appearance similarities have been achieved with natural stone, moreover with innumerable characteristics that exceed the performance of marble, granite, travertine and other stones.

The high technical properties of this product (almost zero apparent porosity, and high mechanical strength, and frost and acid resistance), are due to the high level of quality of the raw materials and the extremely technological production process.

In the Argentine Republic, since the opening in 1993 of the first porcelain tile production plant by Zanon Ceramics, the production of this material has increased enormously, with the incorporation of other companies in the production market, which in turn have broadened the supply from anaesthetic point of view, to the point of obtaining the greatest consideration from the consumer public.

The composition of the body of this material is based fundamentally on three raw materials: plastic clays (ball clays) which contribute the necessary plasticity for forming in the green state and assure the mechanical strength of the pieces in drying; sodium-potassium feldspars that provide the first liquid phases to appear in firing, which initiate the densification process and contribute most to reducing tile porosity; and finally quartz sands that are used for the physical and chemical fit of the body.

Today's great challenge for the mining industry in Argentina, in order to provide raw materials with the quality and homogeneity that the present level of the ceramic industry requires, fundamentally involves performing profound research into the existing raw materials and subsequently, selecting those that embody the best qualities to be used individually, or developing mixtures with some of those that display all the properties that top-level technology demands.

The objective of this study has been the development of porcelain tile bodies, formulated with raw materials of Argentine origin, selected and treated in combination with materials of Spanish origin, lowering the cost of the finished product.

2. METHODOLOGY

The physico-chemical, mineralogical and technological study has been performed of a group of selected raw materials, involving Argentine kaolinitic clays and bentonites, and quartz sands and sodium-potassium feldspar with low iron content of Spanish origin, examining their potential application in porcelain tile bodies. After their characteristics had been studied, porcelain tile bodies were formulated with these raw materials and sludge wastes from the ceramic tile production process.

The properties of the resulting ceramic bodies have been evaluated by several characterisation studies: structural, microstructural; closed and apparent porosity, and mechanical strength. The characterisation techniques used have been:

- **X-ray fluorescence (XRF):** For the chemical analysis of the samples a BRUKER model S4 Pioneer wavelength-dispersive X-ray fluorescence spectrometer has been used.
- **X-ray diffraction (XRD):** A Bruker model D4 diffractometer has been used. The measurements were made at an intensity of 20 mA and a voltage of 40kV, in a 2θ range of 5 to 70°. The counts were made in 3 second steps and the goniometer velocity was 0.050° 2θ /s. This technique has been used to determine the crystalline phases present in the materials used.

- **Scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX).** For the microstructural analysis of the prepared porcelain tile test specimens a LEO model 440i scanning electron microscope has been used with energy-dispersive X-ray microanalysis, with an Oxford model Linx-ISIS instrument with backscattered and secondary electron detector. The conditions used for obtaining the different microanalyses have been an alteration voltage of 20 kV and current intensity in the filament of 2000pA.

The characterisation of the raw materials was performed at the CIDEMAT laboratories, in the Institute for Mining Technology (INTEMIN-SEGEMAR) and the development and characterisation of the porcelain tile bodies were conducted at the laboratories of the Central Scientific Instrumentation Service (SCIC), of the Department of Inorganic and Organic Chemistry of Universitat Jaume I, Castellón, with the collaboration of the company Tierra Atomizada S.A.

3. EXPERIMENTAL DEVELOPMENT

3.1. CHARACTERISATION OF THE RAW MATERIALS

3.1.1. Chemical analysis.

The raw materials of Argentine and Spanish origin have been characterised. Table 1 details in percentage form, the chemical composition of the raw materials. The analysis of the samples was made with the wavelength-dispersive X-ray fluorescence spectroscope technique. The samples were prepared according to the fused bead technique, with lithium tetraborate.

SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	LOI
Clay 1	71,2	18,8	0,87	0,45	0,51	0,40	0,40	2.15	0.10	5,78
Clay 2	68.70	20.4	0,90	0,46	0,47	0,34	0,38	2,61	0.13	5,60
Clay 3	69.90	19.90	0.67	0,51	0,36	0,11	0,30	1.99	0.20	5,82
Clay 4	69.00	18,9	0,76	0,59	0,50	0,45	0,35	1.97	0.10	5,95
Bentonite CH	67.80	13.3	1.20	0,17	1,78	3,75	1,60	0,34	0.02	5.84
Spanish sodium-potassium feldspar	68.6	17.2	0.17	0.03	0.43	0.05	2.58	10.80	0.05	0.32
Feldspathic sand	92.3	4.56	0.21	0.07	0.040	0.04	0.000	2.78	0.000	0.64
*Waste sludge	56.70	16.90	1.64	0.33	5.14	1.04	3.02	1.97	0.00	3.54
*Waste sludge	BaO	PbO	ZnO	ZrO_2	SnO_2	MnO	SrO			
	1.57	0.62	3.50	4.55	0.06	0.01	0.03			

Table 1. Chemical analysis of the raw materials of Argentine origin.

3.1.2. Mineralogical analysis.

The mineralogical composition was studied by X-ray diffraction on powder using a Philips PW 4070 diffractometer for the Argentine samples and a BRUKER D4 instrument for the Spanish samples. The identified crystalline species appear in table 2.

SAMPLE	MAIN COMPONENT	SMALLER COMPONENT
Clay 1	Quartz, kaolinite, sodium-calcium	Pyrophyllite, Muscovite
Clay 2	Quartz, kaolinite, albite, anorthite	Pyrophyllite, Fosterite
Clay 3	Quartz, kaolinite, sodium-calcium	Muscovite
Clay 4	Quartz, kaolinite, sodium-calcium	Muscovite
Bentonite CH	Montmorillonite, illite, Imogolite	Quartz
Spanish sodium-potassium feldspar	Microcline, albite	Quartz
Feldspathic sand	Quartz	microcline
Industrial waste	-	-

Table 2. Mineralogical analysis of the raw materials of Argentine origin.

The results obtained in the chemical and mineralogical analysis show the similarities present between the clays of Argentine origin, which all have a very similar oxide composition and the same crystalline phases. Note that the clays of Argentine origin have a high quartz content, which will contribute high dimensional stability to the fired ceramic body.

3.1.3. Particle size distribution.

The particle size distribution of Argentine clays has been measured (table 3). The test was performed with a Sedigraph 5100 instrument. The sample was previously dispersed in water by stirring, with a calgon addition.

	Sample 1	Sample 2	Sample 3	Sample 4
Diameter (μm)	Cumulative through weight %			
63	94,99	95,1	94,3	97,5
60	94,99	95,1	94,3	97,5
50	94,99	95,1	94,3	97,3
40	94,99	95,1	93,8	96,5
30	94,32	94,8	91,7	94,7
25	93,46	93,6	89,0	92,7
20	91,16	91,0	84,2	88,5
15	86,77	84,8	80,2	82,8
10	79,60	72,9	71,3	74,1
8	75,97	66,4	63,5	67,3
6	71,86	58,5	58,2	59,4
5	68,8	54,1	53,8	54,6
4	64,03	48,3	47,8	48,9
3	57,24	40,2	40,3	41,5
2	47,21	32,4	33,1	33,7
1,5	41,95	27,8	28,9	29,2
1	39,80	25,3	26,6	27,7

Table 3. Particle size distribution of clays measuring cumulative through weight %.

The data corresponding to the particle size distribution of the clays indicate that, in spite of their high content in non-plastic raw materials: quartz and feldspathic phases, these are of fine particle size. The fineness of these clayey raw materials is responsible for the fluxing behaviour of these clays.

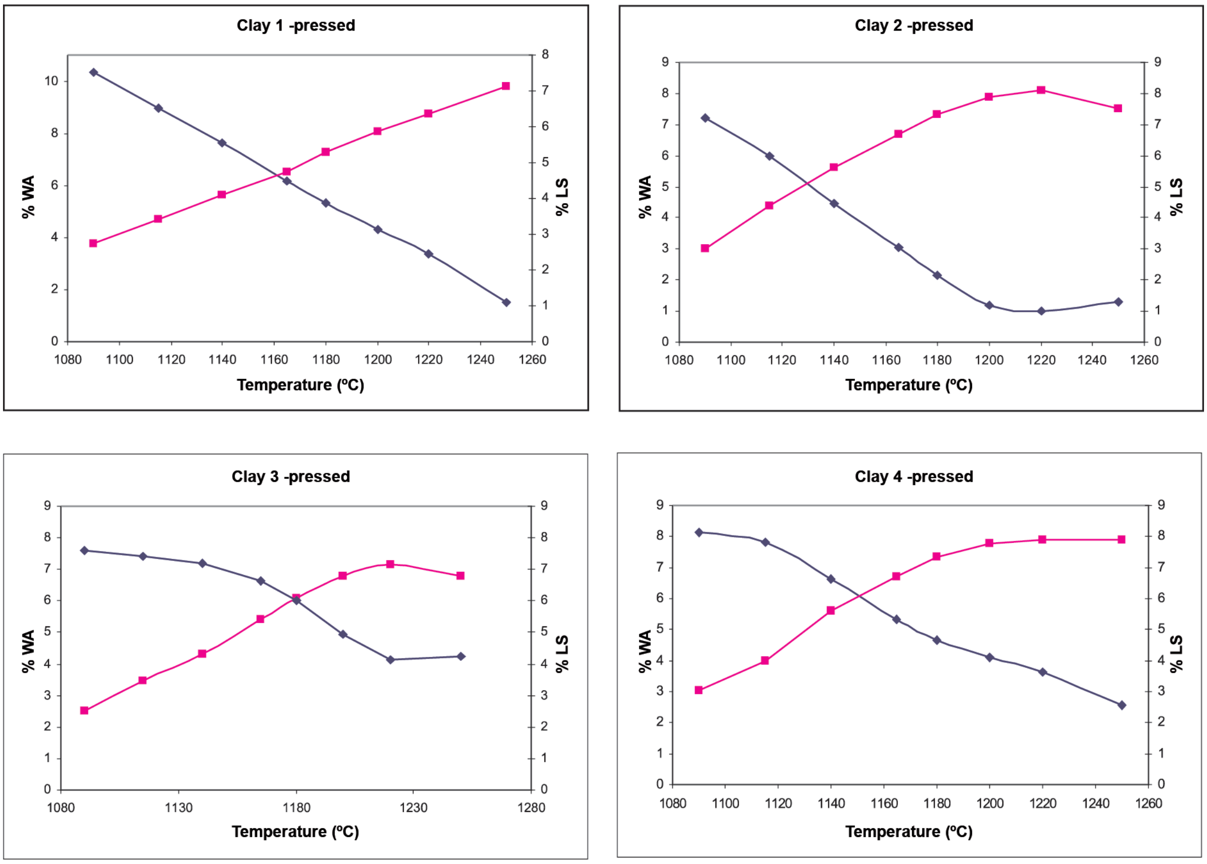
3.1.4. Rheology. Deflocculation curves.

A Brookfield viscometer was used for the determination of the rheological behaviour of the Argentine clays, with a rotation speed of 10 rpm and no. 5 needle. A commercial product with humic acids and sodium silicate was used as a dispersant. Table 4 details the results.

SAMPLE	Minimum viscosity (cp)	Density (g/cm^3)	Dispersant (%)
Clay 1	800	1,56	0,3
Clay 2	2100	1,61	0,2
Clay 3	400	1,59	0,25
Clay 4	680	1,62	0,2

Table 4. Distinctive parameters of the rheological behaviour of the clays.

3.1.5. Vitrification diagrams of the clays



Figures 1-4. Vitrification diagrams of the clays formed by pressing.

Finally, test specimens were prepared by both pressing and moulding. Pressing was conducted at a pressure of 200 kg/cm^2 and 10 % water. The moulded test specimens were prepared at 21% water. All the test specimens were calcined with a porcelain tile firing cycle to temperatures between 1090 ºC and 1250ºC, with a dwell time at peak temperature of 30 min. Figures 1-4 show the corresponding vitrification diagrams of the clays.

The vitrification diagrams corroborate what has been remarked previously: clays 1-4 are quite fluxing with quite wide ranges of stability.

3.1.6. Mechanical properties of the clays.

Finally the mechanical properties of clays were evaluated, in particular, the dry bending strength of the test specimens calcined according to standard DIN 51030. The test specimens were prepared by moulding in the plastic state with 20% water.

Sample	Clay 1	Clay 2	Clay 3	Clay 4
Bending strength	3,60	2,53	1,96	2,16

Table 5. Bending strength (MPa).

3.2. CHARACTERISATION OF THE PORCELAIN TILE TEST SPECIMENS

3.2.1. Preparation of the compositions.

Different porcelain tile compositions were prepared. The procedure followed is described below.

Milling the non-plastic raw materials (quartz and potassium feldspar) in a planetary mill with alumina balls for 54 min., and milling for an additional 6 minutes of the clays, bentonite and waste sludge. The resulting slurries were controlled, obtaining values for the reject at 63 µm of 1-1,5%, density 1,71 g/cm^3 and solids content 67%. The slurries were dried in a laboratory oven at 110 ºC. The resulting ceramic material was crushed in a blade mill and sieved at 1mm. Table 6 shows the prepared compositions.

Raw material	Formulation P0 (%)	Formulation P1 (%)	Formulation P2 (%)	Formulation P3 (%)	Formulation P4 (%)
Clay 1		40	-	-	-
Clay 2		-	40	-	-
Clay 3		-	-	40	-
Clay 4		-	-		40
National feldspar	40	40	40	40	40
Feldspathic sand		12	12	12	12
Bentonite		3	3	3	3
Waste sludge		5	5	5	5

Table 6. Prepared porcelain tile compositions.

3.2.2. Vitrification diagrams of the porcelain tile test specimens.

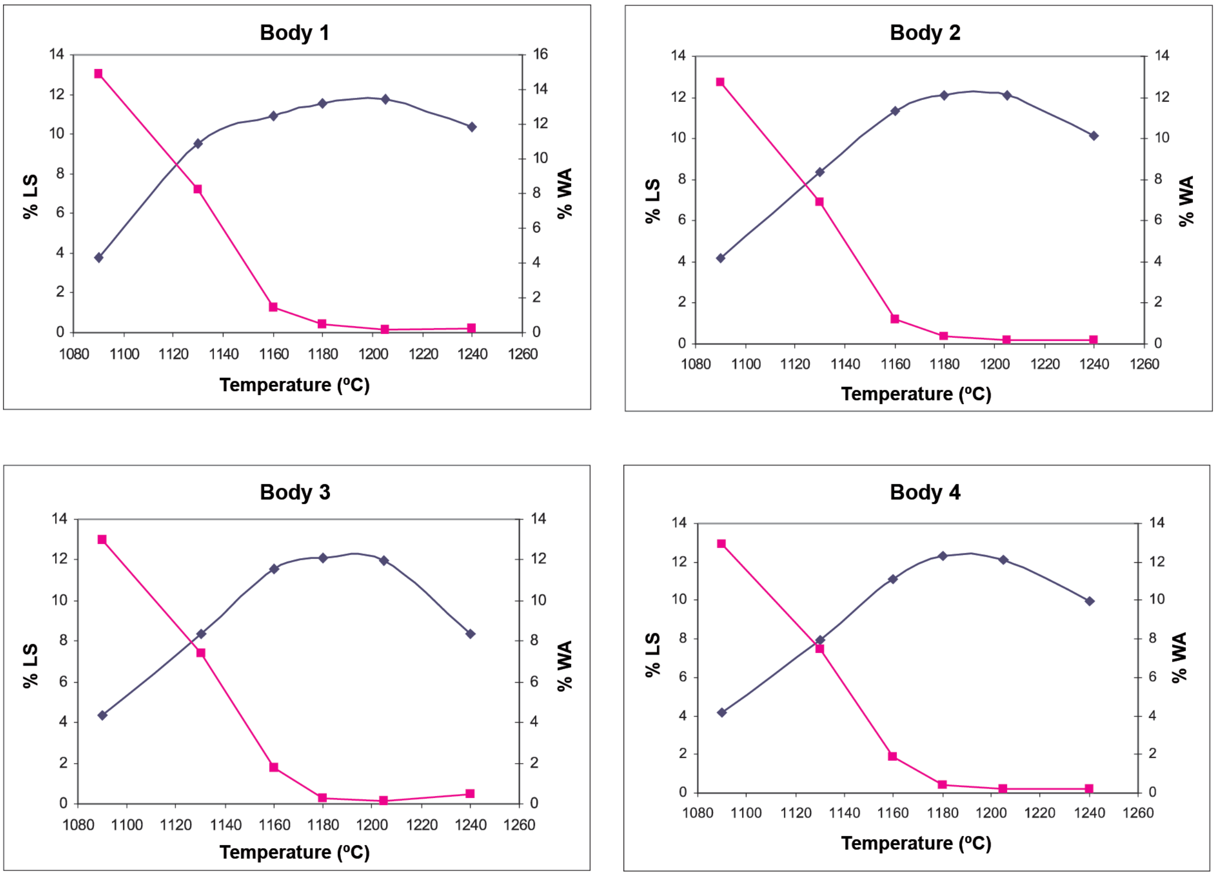
The ceramic powder was then pressed to a green bulk density of 1,91 g/cm^3. The test specimens were dried in a laboratory oven at 110 ºC. The calcination of the porcelain tile test specimens was done in an electric laboratory kiln using a firing cycle of 62 min. and dwell of 6 minutes at $T_{maximum}$, shown in table 7:

Temperature (ºC)	1-500	850	980	$T_{MAX.}$	$T_{MAX.}$	680	500	30
*Time (min.)	5	6	6	10	6	11	8	10

** These correspond to rise times up to the indicated temperature.*

Table 7. Firing cycle in an electric laboratory kiln for porcelain tile bodies.

The vitrification diagrams of the formulated porcelain tile bodies are displayed below, in which it can be observed that at working temperatures between 1180 and 1210ºC they all exhibit low values of apparent porosity and high dimensional stabilities.



Figures 5-8. Vitrification diagrams of the porcelain tile compositions formed by pressing.

3.2.3. Mechanical properties of the porcelain tile test specimens.

The effect of including the Argentine bentonites on the green mechanical properties of the bodies was determined by measuring the dry bending strength according to standard UNE-EN ISO 10545-6:1998.

Test specimens of each of the bodies were fired at 1190 ºC, as this was considered the optimum work temperature, and bending strength was determined according to standard UNE-EN ISO 10545-6:1998. The results are given in table 8.

Composition	P0	P1	P2	P3	P4
*Green bending strength (N/mm^2)	2.5±0.2	2.6±0.3	2.1±0.1	2.7±0.2	2.6±0.1
*Fired bending strength (N/mm^2)	42.21±0.4	36.92±0.6	37.69±0.4	36.97±0.3	42.14±0.8

Table 8. Bending strength of the dry test specimens and after firing at 1190ºC (N/mm^2).

It should be noted that the results obtained in the trials performed on test specimens fired in a laboratory kiln are usually lower than those in the industrial trials, but even so they will enable us to compare the mechanical properties of reference industrial composition P0 with those of compositions P1, P2, P3, P4 and allow evaluating the effect that the bentonites have on the mechanical behaviour of the test specimens.

3.2.4. Colorimetric analysis of the porcelain tile test specimens.

Given the importance attached to whiteness in porcelain tile bodies, an analysis was performed of the CIE-Lab chromatic coordinates of the test specimens fired at 1190 ºC in a CARY Scan, model VARIAN 500, UV-Vis-NIR spectrometer.

Sample	P0	P1	P2	P3	P4
L*	66.4186	71.3300	65.5155	67.0745	68.2253
a*	3.3083	3.3563	4.4293	4.4033	3.8816
b*	12.4778	10.3407	9.1300	9.2581	9.5083

Table 9. Analysis of the CIE-Lab chromatic coordinates of the test specimens fired at 1190ºC.

The values obtained for the 4 compositions were compared with those of an industrial references sample, P0. The values in table 9 show no significant changes in the colour of the test specimens. Since glazed porcelain tile has a much greater degree of tolerance than technical porcelain tile or unglazed porcelain tile, these raw materials are considered excellent for the production of glazed porcelain tile.

3.2.5. Microstructural analysis of the porcelain tile test specimens.

Finally, microstructural analysis has been performed of the reference composition P0 and of compositions P1, P2, P3, P4 prepared with Argentine and Spanish raw materials, in which the closed porosity present in the ceramic body of the test specimens can be observed. Figures 9-13.

The images obtained by SEM with a secondary electron detector of the polished surface of a cross-section of the fired bodies P0, P1, P2, P3, P4 at 1190 ºC show that no great differences are detected between the prepared formulations and the reference composition. The amount of closed porosity in all of these does not appear to be excessively high. The results confirm that these raw materials, as far as the resulting porosity is concerned, are appropriate for the production of technical porcelain tile.

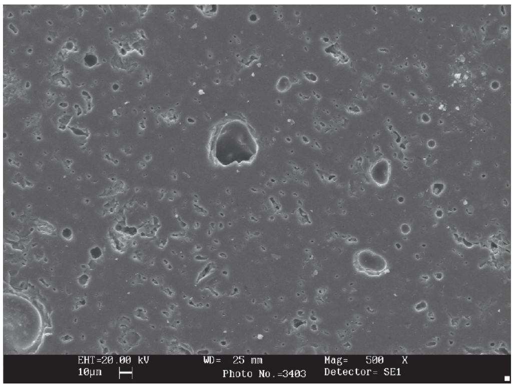


Figure 9. Micrograph (SEM/EDX) of the polished surface of sample P0 fired at 1190 ºC.

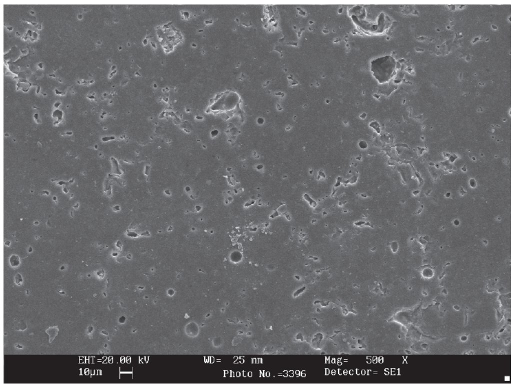


Figure 10. Micrograph (SEM/EDX) of the polished surface of sample P1 fired at 1190 ºC.

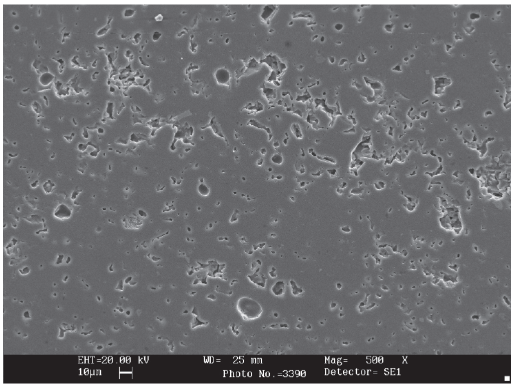


Figure 11. Micrograph (SEM/EDX) of the polished surface of sample P2 fired at 1190 ºC.

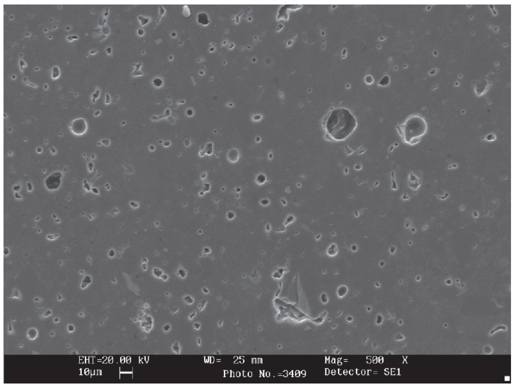


Figure 12. Micrograph (SEM/EDX) of the polished surface of sample P3 fired at 1190 ºC.

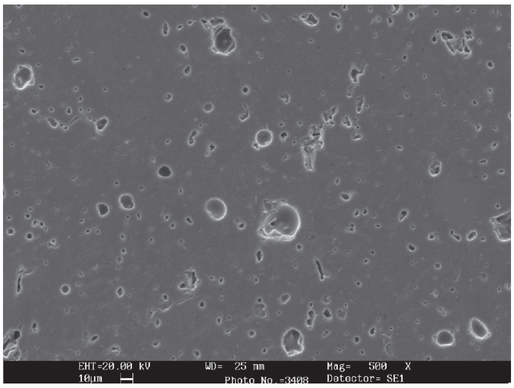


Figure 13. Micrograph (SEM/EDX) of the polished surface of sample P4 fired at 1190.

4. CONCLUSIONS

- Porcelain tile body compositions have been formulated with Argentine and Spanish raw materials: Argentine clays and bentonites, and Spanish feldspathic sands and sodium-potassium feldspars.
- The modulation of the body compositions formulated with the introduction of sludge from industrial ceramic wastes has been completed.

- The introduction of bentonites of Argentine origin evidenced a clear improvement of the mechanical strength in the green pressed test specimens, and did not appear to affect significantly the after-pressing expansion of the test ceramic specimens.
- The apparent dimensional stability and the good fluxing behaviour of Argentine clays enable obtaining compositions with high dimensional stability and low apparent porosity.
- The fluxing behaviour of clays is completed with the incorporation of the sludge, which has facilitated the introduction of Spanish sodium-potassium feldspars, replacing the traditional imported sodium feldspars, and thus making it possible to lower the cost of the formulated porcelain tile bodies.
- The results of the colorimetric analysis indicate comparatively higher whiteness values than those of a conventional porcelain body.

5. ACKNOWLEDGEMENTS

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